Number 9
September, 1961

BULLETIN OF THE ACADEMY OF SCIENCES

OF THE USSR

Division of Chemical Science

(IZVESTIYA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
No. 1 *Jan.-Feb. 1952*

	U. S. and Canada	*Foreign*
Annual subscription	*$120.00*	*$125.00*
Annual subscription for libraries of nonprofit academic institutions	*30.00*	*55.00*
Single issue	*15.00*	*15.00*

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THE 100th ANNIVERSARY OF THE THEORY OF CHEMICAL STRUCTURE

G. V. Bykov

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1533-1538, September, 1961

In the seven-year plan for the development of the national economy, adopted by the XXIst Congress of the Communist Party of the Soviet Union, an important place was given to the development of chemical science and chemical industry. The Congress also pointed out the necessity for every possible extension of theoretical studies in the field of chemistry, without which no successful solution can be found for the many varied problems concerned with the production of new synthetic materials with desired properties, the development of new technological processes, and the improvement of existing processes, and without which the creative development of chemical science and industry in general is impossible. In the resolution of the Central Committee of the Communist Party of the Soviet Union and the Council of Ministers of the USSR, dealing with the activities of the Academy of Sciences of the USSR, mention was also made of the need to concentrate the efforts of Soviet scientists towards finding a solution for the major theoretical problems which are of fundamental importance for the development of the main trends in science.

In the Draft Program of the Communist Part of the Soviet Union, the development of theoretical studies in the main branches of natural science is regarded as one of the most important problems of science in the Soviet Union. The leading branches of natural science referred to in the program include chemistry.

One of these most important theoretical problems in chemistry is the development of the modern theory of chemical structure—that is the development of theories dealing with the structure of chemical compounds and the relationship existing between their properties and their structure, which research chemists could use with a success equal to that with which others in their time applied the classical theory of chemical structure. For the characterization of the present state of the theory of structure in chemistry, A. M. Butlerov's statement of 100 years ago is quite appropriate: "Today, following the discovery of a mass of unexpected and important facts, almost everyone recognizes that the theoretical side of chemistry does not correspond to its factual development". And in another place: "This transitional state of our science gives rise to a mass of private theoretical opinions and different methods of expressing them". The transition state to which A. M. Butlerov referred ended with the creation of the theory of chemical structure.

The 19th of September, 1961 marks the 100th anniversary of A. M. Butlerov's report to the Congress of German Naturalists and Physicians at Speier, in which the fundamental hypotheses of this theory were formulated for the first time. The 19th of September, 1861, can therefore be regarded as the date of the introduction of the chemical structural theory itself. While noting this extremely important event in the history of chemistry, we shall find it appropriate not only to remember it in its purely historical aspect, but also to examine, as far as possible, the significance of the ideas and methods of the classical theory of chemical structure at the present time.

The starting points for the creation of a theory of chemical structure were provided by the concept of valence ("atomicity") and in particular the tetravalence of carbon atoms (the main credit for the introduction of this concept belongs to A. Kekule—1857 and 1858), the concept of an interatomic bond and in particular the idea of the possible formation of carbon chains (these ideas were put forward almost simultaneously in 1858 by A. Kekule and A. S. Couper), and the formulation of an accurate picture of atoms and molecules with the simultaneous elimination, from formulae, of symbols corresponding to equivalent weights. This prolonged process, which began with the work of C. Gerhardt and A. Laurent, was completed at the International Congress of Chemists at Karlsruhe in 1860.

In the report cited, A. M. Butlerov formulated the concept of chemical structure on the basis of these hypotheses of chemical theory, which at that time were comparatively new and unestablished: "Assuming that to each chemical atom there corresponds a characteristic, definite, and limited amount of chemical force (affinity), with which it takes part in the formation of a body, I would use the term "chemical structure" to denote this chemical bond or

means by which atoms combine with one another in a complex body"*. In this definition A. M. Butlerov on the one hand summarized, as it were, the whole of the previous development of the science and, on the other, placed before chemists a new task—the study of the chemical structure of chemical compounds. The extremely important hypothesis of the classical theory of chemical structure, which he later formulated —"The chemical nature of a complex particle is determined by the nature of the elementary component parts , their quantity, and by the chemical structure"—opened the way to considerable development in this direction. The above hypothesis means that it is possible to establish the chemical structure of a substance from its chemical properties and, having determined its structure, to obtain information on the other properties of the compound and substances of analogous structure.

The determination of the chemical structure of organic compounds was a practical task which could be achieved by chemical methods, in contrast to the task, quite impossible at that time, of establishing the relationship between the spatial arrangement of atoms and the properties of substances. At the same time Butlerov never rejected the possibility that a knowledge of the three-dimensional structure of molecules could be obtained and he even opposed those chemists who rejected such a possibility on principle. In his report Butlerov showed that in order to reach conclusions regarding chemical structure it is possible to use all types of chemical reaction: synthesis, decomposition, and substitution. He also stated that in the future, by making a detailed study of the chemical structure of substances, chemists would be able to reach conclusions regarding the mutual influence of atoms in molecules and the rearrangements taking place during chemical reactions.

The history of organic chemistry confirms the complete accuracy, far-sightedness, and fertility of the fundamental hypotheses which were put forward by Butlerov in his report and which, taken together, made up the classical theory of chemical structure. The views of Butlerov, as is often the case with those who break with established traditions, were not however accepted at first. He had to defend and develop them further almost alone. In 1863, Butlerov provided a solution to the most difficult problem of that time—he explained the phenomenon of isomerism. He pointed out for the first time that, as a result of the difference in chemical structure and the consequent difference in the mutual influence of the atoms in the molecules of isomers, the "chemical value" of the elementary atoms and groups in the latter were not identical, so that isomeric compounds exhibit different properties. This work of Butlerov's attracted the attention of chemists and the following is a typical result: in the 1st edition of the 2nd volume of his textbook published in 1863, Kekule used complex types exclusively, but in the 2nd edition of the same book (published in 1864) he abandoned them. Of particular importance in the victory of the ideas of the theory of chemical structure was the experimental work of A. M. Butlerov. In 1864, he prepared trimethylcarbinol and interpreted isomerism in the series of saturated alcohols. In the same year, in contradiction of the opinions of Wurtz and Schorlemmer, he predicted the existence of isomerism in the saturated hydrocarbons. In 1865, Butlerov showed the existence of isobutylene. In the same year he reported the preparation of the three higher homologs of trimethyl carbinol, which he had predicted, in 1866 he reported the preparation of isobutane, and in 1867 the preparation of isobutylene. The theory of chemical structure was thus brilliantly confirmed by experiment and by the second half of the sixties it had become the reigning theory of organic chemistry; chemists directed their efforts towards the study of the chemical structure of the many substances then known and the preparation of new substances, with the theoretical formula of chemical structure as a guide. In 1865 special fruitful hypotheses regarding the structure of aromatic compounds (by Kekule) and unsaturated aromatic compounds (by Erlenmeyer) were put forward.

In the seventies the theory of chemical structure underwent important further development. "Facts which cannot be explained by existing theories are most dear to science", wrote Butlerov; "it is from the solution of these problems that we can expect the greatest development of science in the near future". In fact, as the chemical structure of an ever-increasing number of organic compounds was studied, there was a rapid accumulation of facts which contradicted the hypothesis that the molecules of isomers should always have a different distribution of the bonds between the atoms, i.e., it was found that in some cases the theoretically-predicted number of isomers for a given formula was less than the number of isomers actually found. A great deal of work was done on the study of the isomerism of fumaric and maleic acids, which contradicted this hypothesis, and also on the study of the many cases of optical isomerism. The extensive generalization of the facts known at that time regarding such isomerism, and the bold hypothesis put forward to explain them, made it possible for J. H. van't Hoff, in 1874, to lay the foundations of "chemistry in space", subsequently known as stereochemistry. The extent to which the time was ripe for the new theory can be judged from the fact that slightly later in the same year, the same ideas, but with less sweeping and bold conclusions,

* One year later, in a Russian version of the report, A. M. Butlerov gave an analogous definition of the concept of chemical structure (see A. M. Butlerov, Works, Vol. 1, Acad. Sci. USSR Press, Moscow, 1953, p. 70).

were put forward by J. Le Bel.

In the following 40 years, organic chemistry developed rapidly, based on the theory of chemical structure. Tens of thousands of new compounds were synthesized, and these found application far beyond the walls of scientific laboratories; a fundamentally new method for systematizing organic compounds was created, its foundations laid by Butlerov in his classical "Introduction to the Complete Study of Organic Chemistry"; a successful attempt was made to develop a rational nomenclature for organic compounds; and phenomena relating to the topics of tautomerism and irreversible isomerisation were generalized and to some extent explained.

With the passage of time, moreover, many new problems arose, related primarily to the explanation of the mechanism of the mutual influence of atoms, and in this field the first generalizations were made in the sixties by A. M. Butlerov and his eminent successor V. V Markovnikov. The classical hypotheses of the theory of chemical structure, in spite of the development due to J. Thiele, could not explain many features of the structure and properties of aromatic and unsaturated aliphatic compounds with conjugated multiple bonds. The electronic theories which arose during the first decades of the present century answered, or at least attempted to answer, many of these problems, and a particularly successful achievement of theoretical chemistry in the XXth century was the development of quantum-mechanical theories of the chemical bond. It is quite evident that the significance which chemists attached to the concept of chemical structure was extending continuously. Stereochemistry introduced the idea of the directional properties of bonds in space and physical methods of study made it possible to determine valence angles and interatomic distances, expressed in absolute units. Quantum mechanics made it possible to discuss the distribution of electron density in a molecule and even to calculate this distribution for the simplest molecules. When applied to more complex molecules, including all organic compounds, however, quantum-mechanical methods, due to their complexity, had and still have to be used with the introduction of additional assumptions (whose influence on the final results of the calculations cannot be estimated), while it is also necessary to use values of certain parameters obtained from experimental data. This constitutes the main reason for the existence in modern chemistry, as in the period before the introduction of the theory of chemical structure and in the words of the founder of this theory, of "a mass structure of individual theoretical opinions and different methods of expressing them".

It is true that the present "transitional state" in the theory of the structure of chemical compounds differs in several respects from that which existed 100 years ago. Firstly, at the present time all directions of development in the theory of structure are based on the same foundation—on the classical theory of chemical structure and stereochemistry, which have both stood the test of time. Secondly, in order to solve structural problems at the present time it is possible to make use of the powerful methods of modern physics, both experimental, in the form of the many physical methods of study, and theoretical, in the form of different quantum-mechanical models and methods of calculation. Thirdly, since the modern theory of structure is acquiring, to an ever-increasing extent, all the more distinct features of a physical theory, it is undergoing a transition from a qualitative theory to a quantitative theory. Butlerov predicted, as early as 1858, that theoretical chemistry would develop in this direction: "Experimental studies will provide us with the basis for a true chemical theory, which will be a mathematical theory of the molecular force which we call chemical affinity. Since, however, affinity is responsible not only for the changes but also for the definite grouping of the elementary atoms in a chemically complex molecule, it should be studied not only during the molecular movement which it produces, but also in the equilibrium state of matter. Up to the present time there has not been nearly enough of this type of study of those physical properties of substances which are not related to the breakdown of molecules and which are capable of providing us with the means for an intensive study of this grouping". In spite of this difference between the state of the theory of structure at the present time and that of a hundred years ago, it is undoubtedly worth while to examine the classical theory of chemical structure in order to find, in its history, examples of the solution of problems analogous to those of today.

A true materialist, A. M. Butlerov emphasized repeatedly that the ideas of chemists regarding atoms and molecules are not fiction, but have a definite relationship to that which actually exists. He opposed attempts to treat symbols in chemical formulae as merely "thinking tools", arising only as a result of "arithmetical operations". Apropos of this subject, Butlerov stated: "What do "arithmetical operations" mean in realistic science, if they do not correspond to anything objective, existing in nature?" He repeatedly had to argue with those chemists who, from positivistic standpoints, rejected or underestimated the part played in science by hypotheses and theoretical considerations in general.

These pronouncements by A. M. Butlerov formed the basis on which Soviet chemists relied in the discussion of the theory of resonance, particularly at the All-Union Conference on the Theory of Chemical Structure in Moscow in

June, 1951. We know now, even from the words of L. Pauling, the founder of the theory, that the initial idea which regarded the theory of resonance as a quantum-mechanical theory was erroneous. The method used in the theory of resonance to express the real structure of molecules, involving the superposition of ideal structures by means of more or less complex "artithmetical operations", could only lead to a vast number of speculative conclusions. The latter, as in the theories which A. M. Butlerov opposed in his lifetime, were somehow or other adjusted to suit the experimental data. The objectivization of these ideal structures, which many chemists approached unwillingly, appeared in a philosophical plan as the purest water of idealism. The pragmatic assertion that the subjective and arbitrary nature of the theory of resonance is justified by its "convenience" and "usefulness" cannot be substantiated, if only for the reason that the theory of resonance has retarded the search for and development of the present promising directions of approach in theoretical organic chemistry, and this, in the case of this branch of chemistry, cannot be regarded as either "convenient" or "useful". The theory of resonance is now disappearing from the scene, and this can only be regarded as a victory for the principles which guided A. M. Butlerov in theoretical chemistry.

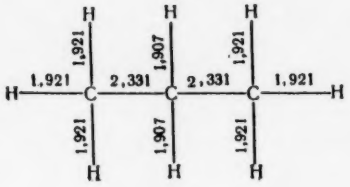
Mention must also be made of certain other features of A. M. Butlerov's approach to theoretical problems. An example is the procedure which he adopted in formulating and solving theoretical problems. First of all the study of the fundamental relationship between the properties and the chemical structure, followed by the study of relationships of secondary character, between the properties of the molecules and the spatial arrangement of the atoms, the manifestation of the mutual influence of atoms not directly joined, etc. From this point of view we cannot regard as completely satisfactory the state of affairs in which most attention in modern theory of structure is paid to the study of "the chemistry of the π-electrons", sometimes in very complex molecules, while the distribution of the σ-electrons in the molecules and its influence on the properties are insufficiently studied, and while quantum-mechanical calculations, with a few isolated exceptions, are lacking even for the simplest molecules—that is for those molecules with which A. M. Butlerov considered it necessary to begin any study.

At the present time in the study of chemical compounds, research workers are divided not according to the methods which they use—for the greater the number and variety of methods of approaching an object of study the better—but according to their aims. Some are trying to determine the "order" of bonds and the "free valence number", others are trying to determine different "indices" for bonds and atoms, while others are trying to determine the effective or actual electronic charges of the atoms and bonds. In his report, as we have already mentioned above, A. M. Butlerov pointed out that the chief aim of the study of molecules should be the examination of the fundamental characteristic of chemical structure. Thus at the present time the most correct approach appears to be to determine not the various "indices" but to determine the actual electronic structure, which at this stage in the development of science, can be represented by a model only by allocating a certain fraction of the total electron cloud of the molecules to definite zones (for example the zones of atoms and bonds).

In this connection we are reminded again of the fundamental principle of the theory of chemical structure, according to which the structure can be determined by studying the properties of the molecules on the basis of a knowledge of the relationships existing between them. It is evident that this semiempirical method can find extensive application at the present time. If some sort of relationship exists between the electronic characteristics of atoms and bonds on the one hand and the properties of their structural elements on the other, it is evident that data obtained by physical, physicochemical and chemical methods can be used, with practically the necessary accuracy, to determine the electronic structure of molecules. In some cases at present the semiempirical method can give information which in the cognitive aspect is no less important than the incomparably more complex and laborious quantum-mechanical methods of calculation.

The classical theory of chemical structure led in its time to formulae which were generally understood by all chemists. As A. M. Butlerov stated in his report of 1861, the formula of chemical structure, "when the general laws of the relationship between the chemical properties of a substance and its chemical structure become generally known, will become the expression of all these properties". In exactly the same way the formulae of the electronic structure can and should express the relationship between the structure and properties of molecules even more fully and deeply than the classical structural formulae. For this, however, it is necessary that the formulae themselves should express the results of the quantitative study of the electronic structure of the molecules. This aim can evidently best be achieved by means of the so-called electronic diagrams (but not molecular diagrams with different types of "indices" on the atoms and bonds), in which figures are used to indicate the fraction of the electronic cloud of the molecule in its different zones. Such diagrams, with the further development of this field of study, may also be constructed for molecules in an activated "reaction" state, and also for radicals and ions.

This approach promises to lead to the solution of one of the fundamental problems of modern theory of structure—the elucidation of the internal mechanism of the mutual influence of atoms. Let us give one example. In 1869, V. V. Markovnikov formulated the following rule: ". . . in saturated hydrocarbons, the hydrogens belonging to those carbon shares (atoms—G. B.) which have spent most of their affinity on the bond with other carbons, undergo substitution more readily than the others". According to this rule, substitution in propane takes place most readily at the bond between hydrogen and the secondary carbon atom. In 1955 the electronic structure of propane was calculated, albeit approximately, for the first time by the molecular orbital method. The results of the calculation are shown in the following electronic diagram:



where each figure shows the magnitude of the electronic cloud (in units of electronic charge) belonging to each bond. The diagram shows that the substitution to which V. V. Markovnikov refers takes place predominatly at the bond with the lowest fraction of the σ-electron cloud. This conclusion can be further extended to hydrocarbons in which there are not two forms of C-H bond, as in propane, but several forms differing in structural position and σ-electron charge.

This example provides a good illustration of how modern electronic theories of structure and reactivity represent the further development, extension, and modification of the classical theory of chemical structure, and also illustrates the great distance it has travelled during the 100 years of its existence.

INVESTIGATION OF THE KINETICS OF SORPTION OF WATER VAPOR FROM A GAS-CARRIER STREAM ON TYPE A ZEOLITES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1539-1542, September, 1961
Original article submitted March 27, 1961

The intensive drying of gas mixtures is one of the main fields of application for type A zeolites. It is therefore of interest to investigate the kinetics of water vapor sorption from a gas-carrier stream on granular zeolites. These investigations should give the kinetic characteristics necessary for the design of a sorption apparatus and information on its optimal operating conditions. The investigations, to some extent, should also throw light on the role of secondary porosity in the kinetics of the process, knowledge of which is necessary in order to be able to granulate zeolites efficiently under large scale technological conditions. In this work we were not able to consider all these problems. Instead we limited ourselves in the investigation to the determination of the water vapor diffusion coefficients in type A zeolites which were adsorbing water vapor from a stream of nitrogen. The results obtained were compared with results obtained from vacuum measurements.

EXPERIMENTAL

Type 4A and 5A zeolites, particle diameter 3 mm, made by the Linde Company, and also similar diameters and zeolites to those used by Ya. V. Mirskii (NaA-296 and CaA-297) with an increased secondary porosity voidage, were used in the investigation. The grains were carefully trimed from the face ends and ground to the shape of a cylinder, with its length equal to the diameter.

The adsorbtion kinetics were investigated by the method of sorption weighings under vacuum and dynamic conditions. The method of measurement under vacuum conditions has been described in [1]. The sketch of the apparatus for investigating the kinetics of sorption under dynamic conditions is given in Fig. 1. The main part of the apparatus is a sorption tube in which a grain of the sorbent is suspended on a quartz spiral. The gas-carrier (nitrogen) is supplied from a cylinder. After removing the impurities from the mixtures in columns 1 and 2 with active carbon and phosphorus pentoxide, a part of the stream is led through the manometer 3 into the evaporator containing water 8 and the other (main) part is led through the manometer 4 into the mixer 5. From the mixer the gas stream either flows into the wet and dry bulb hygrometer 6 or into the sorption tube 7. The relative moisture φ of the gas was assumed equal to 0.1 as a consequence of using the two-stage principle of drying, i.e., the usual drying agents (silica-gel and alumino-gel) for removing high moisture contents, and using zeolite to complete the removal of the reduced concentrations of water vapor. The concentration of water vapor was estimated by weighing the amount of water absorbed by a U-tube containing either phosphorus pentoxide or a fine fraction of zeolite. The wet and dry bulb thermometer was used to keep the conditions constant when carrying out the tests. The evaporator, containing water, was placed in a sensitive thermostat and maintained at 20°C. The specific flow rate in the sorption tube was 1-2 l/min·cm^2.

The experiment was carried out in the following order. The sorbent particle, allowed to reach equilibrium with the moisture in an atmosphere of air, was weighed on an analytical balance to 0.1 mg and placed in the sorption tube. A high vacuum was then established in the tube or, if the dehydration was carried out in the gas-carrier stream, nitrogen was passed through the tube at a low flow rate and the temperature was increased to 350°C. The particles were evacuated for 3 hours. The electric furnace was then removed, the sorption tube cooled to room temperature, dry nitrogen was admitted into the tube (by evacuating from a vacuum line) and after waiting 5 to 10

* T. Erashko participated in the work.

minutes, the test commenced, i.e., the gas mixture containing water vapor was admitted. After a definite interval of time the expansion of the spiral was measured. The readings were carried out with the help of a cathetometer with the graticule scale of the eye-piece graduated at intervals of 0.02 mm. The sensitivity of the spiral was 0.03 mg/scale division.

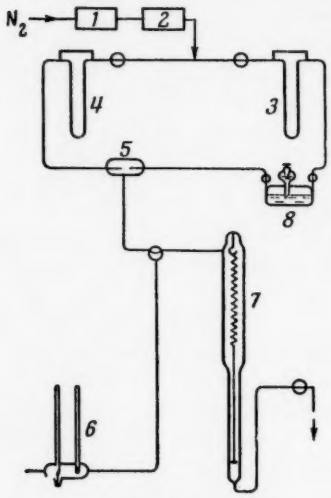

Fig. 1. Sketch of apparatus: 1,2) Columns with active carbon and phosphorus pentoxide; 3,4) Manometers; 5) Mixer; 6) Wet and dry bulb hygrometer; 7) Sorption tube; 8) Evaporator.

The coefficient of internal diffusion D was calculated from the experimental results from the equation for a cylinder of finite dimensions [2]:

$$\gamma = 1 - \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} B_n B_m \exp\left[-\left(\mu_n^2 + \frac{4\mu_m^2}{k^2}\right)\tau\right], \qquad (1)$$

where $\gamma = \frac{a}{a_\infty}$ is the relative adsorption value, a is the adsorption value at the moment of time t, a_∞ is the limiting adsorption value, B_n and B_m are the coefficients determined from the equations

$$B_n = \frac{4Bi_1^2}{\mu_n^2(\mu_n^2 + Bi_1^2)}$$

$$B_m = \frac{2Bi_2^2}{\mu_m^2(Bi_2^2 + Bi_2 + \mu_m^2)},$$

where μ_n is the root of the Bessel function equation $\frac{I_0(\mu_n)}{I_1(\mu_1)} = \frac{\mu_n}{Bi}$; μ_m is the root of the equation $\cot \mu_m = \frac{\mu_m}{Bi}$; Bi_1 and Bi_2 are Biot moduli on the side surface and on the particle end faces; $k = \frac{L}{R}$; $\tau = \frac{Dt}{R^2}$; R and L are the radius and length of the particle.

If we designate $t_{0.5}$ as the time in which the adsorption value γ becomes equal to 0.5 then equation (1) may be converted to the form

$$D = \alpha \frac{R^2}{t_{0.5}},$$

where α is a constant depending on the value of k, i.e., the ratio of the length and radius of the particle (in our case k = 2) and on the Biot modulus. The Biot moduli, expressing the conditions of mass-exchange on the surface of the grain depend on the internal diffusion coefficient and are found by the method of successive approximations.

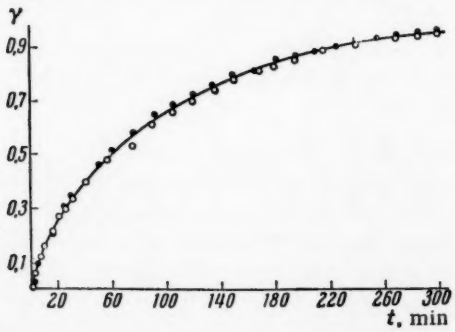

Fig. 2. The sorption velocity of water vapor from a stream of nitrogen on Linde 5A zeolite; ● dehydration in a nitrogen stream; O dehydration in a vacuum.

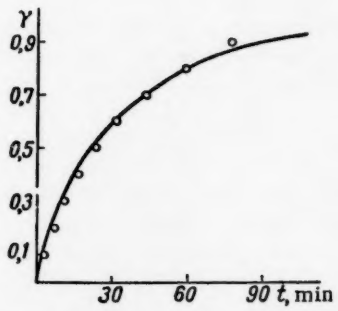

Fig. 3. The kinetic sorption curve from a nitrogen stream on Linde 4A zeolite.

Fig. 2 represents the kinetic adsorption water vapor curves on a molecular sieve of Linde 5A zeolite after dehydration of the sample under vacuum conditions and in a stream of nitrogen. As can be seen from the figure, the experimental points in both cases in practice lie on the same curve, i.e., both methods of dehydration under these conditions give the same results.

TABLE. Diffusion coefficients of water vapor in granular zeolites, type A

Zeolite	$D.10^{-6}$ cm²/sec	
	From the stream	In a vacuum
Linde, 4A	0.51	1.87
Linde, 5A	0.48	1.04
NaA−296	0.73	2.65
CaA−297	0.49	3.03

Fig. 3 represents the kinetic curve for the adsorption of water vapor from a stream of nitrogen on the molecular sieve Linde 4A zeolite. The curve is calculated from equation (1) with the modulus Bi=7 and the coefficient of diffusion $D=10^{-6}$ cm²/sec; the experimental points which are converted to the value $D=10^{-6}$ cm²/sec, are designated by circles. It should be noted that when the experimental curve is superimposed at the value $D=10^{-6}$ cm²/sec. the time on the abscissa decreases respectively as compared with the usual value by a factor of $D_{exp}/10^{-6}$. As can be seen from the graph, the calculated and experimental results completely coincide. Other samples give analogous results. The table reproduces coefficients of diffusion, calculated from equation (2) for the zeolites which were investigated. The coefficients of diffusion given in the table for the vacuum experiments were obtained with a relative water vapor pressure of $p/p_s = 0.1$.

From the results given in the table it follows that the diffusion coefficients of water vapor in zeolites in the presence of a gas-carrier is substantially lower than in the vacuum tests. This is explained by the fact that, due to the presence of the gas-carrier, the diffusion coefficient is reduced in the secondary pores. From the results of Dubinin and his co-workers [3,4] the most probable equivalent radius of the secondary pores in Linde 4A and 5A zeolites are 0.25 μ, and in Mirskii zeolites 0.5 μ. With the relative water vapor pressure $p/p_s = 0.1$ at 20°C (in a vacuum), the length of the molecular free path is of the order 10μ and consequently, Knudsen diffusion occurs in the secondary pores. The Knudsen diffusion coefficient is expressed by the equation

$$D_K = \frac{2}{3} ur, \qquad (3)$$

where u is the gas-kinetic velocity of the molecules (for water at 20°C, $u = 5.1 \cdot 10^4$ cm/sec), r is the capillary radius. By substituting the numerical values u and r in formula (3) we find that the coefficients of diffusion in the secondary pores are equal to $D_k \approx 1$ and ~ 2 cm²/sec for Linde and Mirskii zeolites, respectively; or if we introduce a correction for the finite length of the capillary by the method of Clausing [5], the values are 0.4 and 0.8 cm²/sec.

By filling the secondary pores with nitrogen (at atmospheric pressure) the water vapor diffusion coefficient in these pores become approximately the same as in an atmosphere of nitrogen, i.e., ~ 0.28 cm²/sec. This value is noticeably less than that estimated in the first case. Since the diffusion coefficients inside the zeolite crystals themselves, which make up the particle, do not depend on the presence or absence of the gas-carrier, then the differences between the diffusion coefficients in the secondary pores in the vacuum experiments and in the experiments on adsorption from a gas-carrier stream must also be the reason for the difference in the value of the total coefficient of diffusion in the particle. From the results given in the table it also follows without exception, that the diffusion coefficients of water vapor in 5A zeolites is slightly less than in 4A zeolites. This condition indicates the fact that the diameter of the entry capillaries in 4A and 5A zeolites is not rate determining in the diffusion of the water molecules.

SUMMARY

1. The kinetics of the sorption of vapors on granular, synthetic type A zeolites from a nitrogen stream was investigated.

2. The water vapor diffusion coefficients in zeolites with adsorption from a nitrogen gas stream is substantially less than the values obtained from vacuum experiments. This difference is explained by an increase in the diffusion resistance in the secondary pores of the particle due to a decrease in the length of the molecular free path in the presence of a gas-carrier (at atmospheric pressure).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE CATALYTIC BEHAVIOR OF NIOBIUM PENTOXIDE DURING VAPOR-PHASE AMINATION OF ETHYL ALCOHOL WITH ANILINE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1543-1548, September, 1961
Original article submitted December 30, 1960

Our previous studies of the catalytic properties of niobium and tantalum oxides established that they possess good dehydrating properties [1], and also that they selectively catalyze vapor-phase dehydration-condensation reactions with the formation of new C—C bonds, for example, the condensation of acetaldehyde into crotonaldehyde [2] with virtually no formation of secondary products. It was of interest to study the condensing properties of these oxides in respect to other reactions, for example, reactions concerned with the formation of C—N bonds, and particularly the formation of N-aliphatic-aromatic amines by the reaction of aniline with ethyl alcohol. The production of N-ethyl-and N, N-diethylaniline is also of practical interest.

Much of the literature concerned with the study of amination reactions in the vapor phase pertains to the production of aliphatic amines by means of the interaction of aliphatic alcohols (and also ethers) with ammonia over various oxides, for example, Al_2O_3, SiO_2, TiO_2, and Fe_2O_3, and also mixtures of them. It is only in the last ten years that many articles and patents have been published, from which [3-10] can be cited as examples. The literature concerned with the study of catalytic vapor-phase amination of alcohols with aniline, with the object of producing N-alkyl derivatives of aniline, refers mainly to the production of N-methyl- and N, N-dimethylaniline [11-18], and N-ethyl-and N, N-diethylaniline [7, 19-25]. One of us, together with Shuikin and Dymov [19], studied the reaction of aniline with ethyl alcohol, with the object of producing N-ethyl-and N, N-diethylaniline, over Al_2O_3 and also over mixtures of catalysts ($Al_2O_3 + Fe_2O_3$, $Al_2O_3 + ZnO$, and $Al_2O_3 + Cr_2O_3$), which showed that the latter are more active than pure Al_2O_3 for this reaction. In other investigations Al_2O_3 was also used in the pure form [12, 14, 17, 20, 21], on asbestos [14], mixed with other oxides, for example, WO_3, TiO_2, and MoO_3 [14, 15], and also with additions of Ca, Zn, Cr, Mg, Fe, or Mn oxides [13]. These reactions were carried out not only under normal flow conditions at normal pressure, but also at increased pressure [20]. As well as alcohols the corresponding ethers were used as alkylating agents in a number of investigations [12, 17, 18, 20, 21]; the stronger methylating action of the ether is emphasized in [17].

A study of the catalytic action of a large number of specimens of Al_2O_3 prepared by different methods, H_3PO_4 on carbon, Al_2O_3 with Cu, kaolin, WO_3 with H_3PO_4, silica gel, silica gel with additions of different Fe, Zn, Ca, Th, Cr, and Mg oxides, and also a variety of materials deposited on asbestos (H_3PO_4, Al_2O_3 with WO_3, $AlPO_4$, and $Al_2(SO_4)_3$), on the reaction between aliphatic alcohols (methyl, ethyl, and others with different chain lengths) and aniline in the vapor phase showed that aluminium oxide is the most effective catalyst for N-alkylation of aniline, all the other catalysts, to a greater or lesser extent, also bring about alkylation in the ring [14]. Japanese acid clay [11] (in this case, as well as $C_6H_5NHCH_3$ a secondary product, $p\text{-}CH_3C_6H_4NH_2$, is obtained), bauxite containing a certain percentage of natural iron oxides [7, 22], silica gel [23], and gumbrin [16] were also used as catalysts for the reaction in question; good yields of N-ethylaniline were obtained as a result of using bentonite [24].

The use of Nb_2O_5 as an amination catalyst was not investigated in any of the works which have been referred to; however, on the basis of previous studies of the catalytic properties of this material, Nb_2O_5 would be expected to catalyze the N-alkylation of aniline, which is indeed what happens, as will be seen below.

EXPERIMENTAL

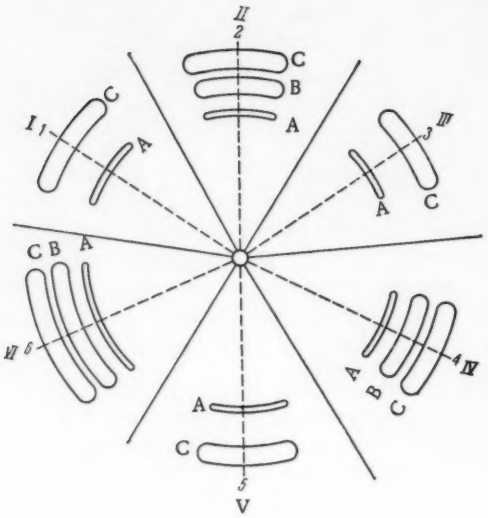
Ethyl alcohol alkylation of aniline experiments were carried out in a normal flow catalysis apparatus [26] over 10 ml (as poured) specimens of the catalysts: powdered Nb_2O_5 and 25% Nb_2O_5 on asbestos, prepared by decomposition of niobium oxalate complex, the appropriate amount of a solution of which had been adsorbed by the asbestos, at 400° C for six hours. Two forms of the powdered Nb_2O_5 were studied: (1) Nb_2O_5 produced by burning metallic niobium in a muffle furnace at 500-530°C for one hour, which was the most active form in respect to the dehydration of alcohols [27], and (2) less active Nb_2O_5 produced by burning the metal at 700-750°C for two hours. Purified and twice-distilled aniline (b.p. 183.5°C (750 mm), n_D^{20} 1.5859) was mixed with redistilled ethyl alcohol (d_4^{20} 0.7914) in 1 : 1 molar ratio. Alternative experiments were carried out with 1 : 1.5 ratio of aniline to alcohol. The aim of the experiments with the mixtures of the components in the 1 : 1 ratio was the directing of the reaction to the formation of n-ethylaniline. The experiments were carried out in the temperature range 350-410°C, and the mixtures were passed at the rate of 0.05 ml/ min, or 0.15 ml/ min in particular experiments, which corresponded to a space velocity of 0.3 hr^{-1}, or 0.9 hr^{-1} in the particular experiments.

Fused KOH was placed in the obtained catalyzate, as a result of which flakes of hydrated alkali separated out. The latter were removed, and KOH was again placed in the catalyzate. The dried catalyzate was distilled from a Favorskii flask fitted with a long fractionating column. In all cases only two fractions were obtained from the distilled catalyzates. The first fraction boiled in the range 75-85°C (up to 95°C in individual experiments), and the second fraction boiled in the range 178-190°C (up to 200°C in the individual experiments). It was mainly the second fraction which was analyzed, and it was shown (see below) that this consisted of a mixture of only N-ethylaniline, a small amount of N,N-diethylaniline, and unreacted aniline; some fractions contained absolutely no N, N-diethylaniline.

Radial paper chromatography [28] was used in order to determine the qualitative characteristics of the composition of the amine mixture in the fraction. Diazodyes derived from the amines were separated. Appropriate conditions were chosen for the separation of the amine mixtures which were obtained in our case. Sulfanilic acid was diazotized, for example, by the method given in [28], and the appropriate amount of diazotized sulfanilic acid was combined with the amine mixture in the catalyzate. Reference-dyes were similarly produced separately with aniline, with N, N-diethylaniline, and with N-ethylaniline. The combining was carried out in the presence of an abundant amount of CH_3COONa, used in order to form a buffer solution at the moment of combination. The solutions were aged for 15-20 min after combination, then one or two drops were applied to the paper in accordance with the pro cedure for radial paper chromatography. A mixture of butanol, acetic acid, and water, in the proportions 4 : 1 : 5, was used as the mobile phase. Two types of chromatographic paper were used: "Whatman No. 1" and "Leningrad High-Speed", which gave practically identical results. The dye produced with N, N-diethylaniline was observed to have the greatest R_f, and the dye produced with aniline—the smallest; the R_f of the dye produced with N-ethylaniline occupies an intermediate position. An example of a chromatogram is shown in figure; the spots on the chromatogram have been outlined with indian ink. On this chromatogram were applied: a mixture of the reference-dyes produced with aniline and N, N-diethylaniline (sectors I, III, and V), and the dyes produced with the amine mixtures obtained in the experiments carried out at 350 and 375°C: A) spots pertaining to the dye produced with aniline; B) spots pertaining to the dye produced with N-ethylaniline; and C) spots pertaining to the dye produced with N, N-diethylaniline.

The spots of the dyes produced with aniline, N-ethyl, and N, N-diethylaniline were of different widths in all cases. Spots of the reference-dyes produced with N, N-diethylaniline (C) and aniline (A) are distributed along the lines 0-1, 0-3, and 0-5; spots of the dyes produced with the second fraction from the experiment carried out at 375°C (Table 1), which, as can be seen, contained only unreacted aniline (A), N-ethylaniline (B), and N, N-diethylaniline (C), are distributed along line 0-2; other aniline derivatives are absent. The spots distributed along line 0-4 similarly correspond to aniline (A), N-ethylaniline (B), and N, N-diethylaniline from the amine mixture obtained from the experiment carried out at 350°C (Table 1); spots of the dyes obtained from the experiment carried out at 350°C are also distributed along line 0-6, but in this case three, instead of two, drops of the dye solution were applied to the chromatogram. The drops of dye produced with aniline are light yellow, with N, N-diethylaniline—orange-brown, and with N-ethylaniline—orange-yellow. It is not possible to detect the intensities of the spots from the printed achromatic figure, but in practice one can easily deduce approximately how much or little of a component is obtained in the mixture, as was confirmed by further qualitative determinations.

The mixtures were qualitatively analyzed for primary, secondary, and tertiary amines by means of a titration method based on the different reactions of primary and secondary amines with nitric acid, and on the combination of diazocompounds which was formed [28]. The experimental results are given in Tables 1-4. As is evident from comparison of the results given in Table 1-3, form (1) of Nb_2O_5 and Nb_2O_5 on asbestos are most active, in respect to the studied amination reactions, in comparison with form (2) of Nb_2O_5, i.e., the catalyst which was least active in respect to the dehydration of alcohols also proved to be least active in respect of the combined dehydration of aniline with an alcohol.



The maximum total extent of the transformations, calculated from the amount of aniline which was passed, in the experiments carried out at 375°C with powdered Nb_2O_5 (form 1) and Nb_2O_5 on asbestos agreed closely and equalled 26.9 and 26.1% respectively, the main product in the mixture being N-ethylaniline (20.7 and 21.0% respectively). The optimum reaction temperature, in the range which was studied, is 375°C for both catalysts. Increase in temperature from 350 to 375°C leads to an increase of the N-ethylaniline content of the catalyzate, and also to some increase of the N, N-diethylaniline content, especially in the case of Nb_2O_5 on asbestos, no N, N-diethylaniline at all being formed over this catalyst at 350°C. Further increase in temperature up to 400°C leads to a decrease in the N-ethylaniline content, and also to a slight decrease in the amount of N, N-diethylaniline, evidently because of intensified decomposition of the ethyl alcohol (see below). Hence, it is obvious, from the experimental results, that change in temperature affects the yield of N-substituted amines, but does not affect the selectivity of the reaction, i.e., the ratio of N-ethyl-and N, N-diethylaniline in the catalyzate; exchange of powdered Nb_2O_5 (form 1) for Nb_2O_5 on asbestos also has practically no effect on selectivity.

TABLE 1.

Amination of Ethyl Alcohol with Aniline over Powdered Nb_2O_5 (form 1). (aniline : alcohol = 1 : 1; mixture passed at rate 0.05 ml/ min; as poured volume of catalyst = 10 ml)

Exptl. temp. (°C)	Amount (ml)			Catalyzate distillation results		Amine fraction composition (by titration) (%)			Extent of transformation from aniline passed %		Extent of transformation from aniline reacted %	
	mixture passed	catalyzate obtained	catalyzate taken for distillation	b.p. of fraction (°C)	amount of fraction (ml)	unreacted aniline	N-ethylaniline	N,N-diethylaniline	N-ethylaniline	N,N-diethylaniline	N-ethylaniline	N,N-diethylaniline
350	30	30	29,5	78,0— 95,0	11,0	71,9	20,6	7,4	15,1	4,4	55,5	15,9
				183,5—186,0	18,5							
375	30	27	26	72,0— 85,0	5,0	64,8	25,6	9,6	20,7	6,2	76,9	22,6
				183,0—189,5	20,5							
400	30	29	27	77,0— 82,0	6,5	69,9	22,2	7,9	17,6	5,0	75,1	21,2
				180,0—188,0	20,0							
375*	32	29	28	78,0— 85,0	6	66,9	24,6	8,5	20,0	5,5	77,1	20,7
				186,0—191,0	21,5							

* After the catalyst had been used (with periodic regeneration) for 30 hr.

In the case of the reaction over the less active form of Nb_2O_5 (powdered form 2) change in temperature from 350 to 400°C has practically no effect on the total yield of N-substituted amines (there is only a somewhat insignificant decrease in yield when the temperature is increased to 400°C), in addition to which the ratio of N-ethyl- to N, N-diethylaniline changes insignificantly in the temperature range which was studied, remaining, on the whole, the same as for the experiments carried out over the other forms of the catalyst. N-ethylaniline is also mainly formed

TABLE 2.

Amination of Ethyl Alcohol with Aniline over Powdered Nb_2O_5 (form 2) (aniline : alcohol = 1 : 1; mixture passed at rate 0.05 ml/ min; as poured volume of catalyst = 10 ml)

Exptl. temp. (°C)	Amount (ml)			Catalyzate distillation results		Amine fraction composition (by titration) (%)			Extent of transformation from anil. passed %		Extent of transformation from aniline reacted %	
	mixture passed	catalyzate obtained	catalyzate taken for distillation	b.p. of fraction, °C	amt. of fraction (ml)	unreacted aniline	N-ethyl-aniline	N,N-di-ethyl-aniline	N-ethyl-aniline	N,N-di-ethyl-aniline	N-ethyl-aniline	N,N-di-ethyl-aniline
				80,0— 90,0	6,5							
350	33	30	29	180,0—188,0	2,5	78,0	15,8	6,2	12,3	3,8	72,7	22,9
				78,0— 88,0								
375	30	29	28	183,0—187,0	19,0	78,7	17,6	3,8	13,3	2,2	72,7	13,3
				77,0— 82,0	6,0							
400	33	30	28,5	175,0—185,0	21,5	81,0	14,3	4,7	11,1	2,0	80,5	20,0
				78,0— 80,0	9,5	12,50	3,11	0,48				
						12,26	3,23	0,51				
375*	30	27	26	179,0—185,0	16,0	76,6	20,2	3,2	12,8	1,6	39,3	5,2

* In this experiment the mixture was passed at rate 0.15 ml/min.

TABLE 3.

Amination of Ethyl Alcohol with Aniline over 25% Nb_2O_5 on Asbestos. (aniline; alcohol = 1 : 1; mixture passed at rate 0.05 ml/ min; as poured volume of catalyst = 10 ml)

Exptl. temp.(°C)	Amount (ml)			Catalyzate distillation results		Amine fraction compostion (by titration) (%)			Extent of transformation from anil. passed %		Extent of transformation from aniline reacted %	
	mixture passed	catalyzate obtained	catalyzate taken for distillation	b.p. of fraction, °C	amt. of fraction (ml)	unreacted aniline	N-ethyl-aniline	N,N-di-ethyl-aniline	N-ethyl-aniline	N,N-di-ethyl-aniline	N-ethyl-aniline	N,N-di-ethyl-aniline
				76,0— 82,0	7,0							
350	30	28	26	180,0—185,0	18,5	82,1	17,9	0	13,1	0	80,0	0
				78,0— 88,0	4,5							
375	30	27	26	178,0—186,0	20,0	64,4	27,5	82	21,1	5,0	74,0	19,5
				78,0— 80,0	6,0							
400	30	27	27	176,0—188,0	20,0	70,0	19,8	10,2	15,7	6,4	67,8	27,5

TABLE 4.

Amination of Ethyl Alcohol with Aniline over Powdered Nb_2O_5 (form 1) (aniline : alcohol = 1 : 1.5; mixture passed at rate 0.05 ml/ min; as poured volume of catalyst = 10 ml)

Exptl. temp.(°C)	Amount (ml)			Catalyzate distillation results		Amine fraction composition (by titration) (%)			Extent of transformation from anil. passed %		Extent of transformation from aniline reacted %	
	mixture passed	catalyzate obtained	catalyzate taken for distillation	b.p. of fraction, °C	amt. of fraction (ml)	unreacted aniline	N-ethyl-aniline	N,N-di-ethyl-aniline	N-ethyl-aniline	N,N-di-ethyl-aniline	N-ethyl-aniline	N,N-di-ethyl-aniline
				75,0— 85,0	10,0							
360	40	39	33	183,0—202,0	22,5	67,8	16,4	15,8	11,1	8,2	29,6	22,3
				79,0— 80,0	3,8							
379	20	19,5	16	183,0—200,0	11,5	55,8	24,8	19,3	17,1	10,4	36,0	22,1
				75,0— 78,0	14,0							
408	40	38	34	180,0—200,0	19,5	68,0	15,9	16,1	9,2	7,3	20,4	16,3

in the reaction. Increase in the rate at which the mixture is passed, from 0.05 to 0.15 ml/min, as is evident from the results in Table 2, causes practically no change in either the total yield or the ratio of N-ethyl to N, N-diethylaniline in the catalyzate.

Change in the ratio of aniline to ethyl alcohol, from 1 : 1.5, as is evident from the results in Table 4, causes a change in the ratio of N-ethyl- to N, N-diethylaniline in the reaction products in favor of an increase in the N, N-diethylaniline content. In this case the yield of N-substituted anilines also passes through a maximum with change of reaction temperature in the range 350-400°C; at the same time, the total percent conversion does not change in comparison to the conversion in the experiments with the other mixture ratio (1 : 1), a decrease in the amount of N-ethylaniline formed being compensated by an increase in the amount of N, N-diethylaniline. In the experiments at 400°C it was observed that a small amount (1-2 ml/min) of gas was evolved, the composition of which (mainly C_2H_4, and small amounts of CO and CO_2) indicates that it forms as result of the partial decomposition of the ethyl alcohol. The duration of catalyst operation should be noted. The catalyst was always regenerated in a current of air at 400°C for 3-4 hr after 20 ml of mixture had been passed; with such periodic regeneration the catalyst retained its initial activity after 30 hr operation (see Table 1, the experiments carried out at 375°C).

We found that tantalum pentoxide acts similarly to niobium pentoxide in the described reactions.

Much of the experimental work was carried out by laboratory assistant Z. M. Skul'skaya.

SUMMARY

1. Niobium pentoxide possesses catalytic activity in respect to the amination of ethyl alcohol with aniline. With a 1 : 1 ratio of aniline to ethyl alcohol in the mixture which was passed the reaction tends mainly to the formation of N-ethylaniline. Change of aniline to alcohol ratio up to 1 : 1.5 causes the amount of N, N-diethylaniline in the catalyzate to increase, the total extent of conversion remaining practically constant.

2. The most active of the catalysts which were studied proved to be powdered Nb_2O_5 obtained by burning the metal at 530° for one hour, i.e., the form of powdered Nb_2O_5 which was most active for dehyration of alcohols.

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THE MECHANISM BY WHICH PROPANE FORMS DURING THE DECOMPOSITION OF ISOPROPYL ALCOHOL OVER VANADIUM TRIOXIDE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1549-1551, September, 1961
Original article submitted February 6, 1961

It is well-known that vanadium oxide catalysts possess dehydrogenating and dehydrating activity in respect to alcohols. A characteristic property of these catalysts is a high paraffinic hydrocarbon content in the catalyzate. Komarewsky [1] found that n-butyl, isobutyl, n-hexyl, and n-octyl alcohols at 380-400°C produce, together with butene, hexene, and octene, considerable amounts (up to 50%) of the corresponding alkanes. It is very possible that the hydrogen liberated by the dehydrogenation of the alcohol, under the conditions of the reaction, promotes hydrogenation of the olefins. It is stated in the literature [2] that alkenes can hydrogenate over catalysts of this type. Furthermore, since a number of authors [3-5] obtained alkanes, the chain lengths of which were one carbon atom less than the original alcohols, it is very possible that alkanes are produced directly from the alcohols by hydrogenolysis of C–O and C–C bonds. In connection with this, the clarification of the mechanism by which saturated hydrocarbons form during decomposition of the alcohols is of considerable interest.

The kinetics of the decomposition of isopropyl alcohol over vanadium trioxide were studied by Balandin and Sokolova [6]. They derived the magnitude of the activation energy for dehydrogenation of the alcohol. In order to determine the dehydration activation energy it was necessary to solve the problem of whether or not propylene is an intermediate product during propane formation. Depending on the solution of this problem, the rate of dehydration should be calculated from experimental data concerning the rate of formation of propylene, or concerning the sum of the rates of formation of propane and propylene. In [6] the magnitudes of the energies of the bonds between the reacting atoms and the catalysts were calculated. With the assumption that propane forms as a result of a secondary reaction–propylene hydrogenation–the bond energies were shown to be

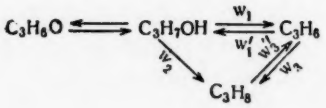
$$Q_{H\text{-}cat} = 54.4; \quad Q_{C\text{-}cat} = 20.6, \text{ and } Q_{O\text{-}cat.} = 44.9 \text{ kcal/mole.}$$

With the assumption that propylene is the end product of the dehydration, and propane is formed by hydrogenolysis, the following values were obtained:

$$Q_{H\text{-}cat.} = 58.5, \quad Q_{C\text{-}cat.} = 16.2, \text{ and } Q_{O\text{-}cat.} = 40.1 \text{ kcal/mole.}$$

The correctness of one or other of the assumptions could be verified with the aid of labeled atoms. Therefore, we decided to use a kinetic method utilizing labeled atoms also to study the mechanism of decomposition of isopropyl alcohol with additions of propylene labeled with radiocarbon-14.

The different mechanisms by which isopropyl alcohol decomposes, under the conditions in question, can be depicted by the following scheme:



The scheme embraces all the theoretically possible reactions. However, at 315°C propane dehydrogenation is improbable ($K_p = 5.6 \cdot 10^{-5}$) and rate W'_3 can be disregarded. In this case the righthand portion of the scheme becomes similar to the scheme for ethyl alcohol decomposition [7], and in order to determine the individual reaction rates the following equations can be used:

$$w'_1 = \frac{d\alpha}{d\tau} \cdot \frac{-c_1}{\alpha - \beta}; \quad w_3 = \frac{c_3 \frac{d\gamma}{d\tau} + (\gamma - \alpha)\frac{dc_3}{d\tau}}{\beta - \alpha}; \tag{1}$$

$$w_1 = \frac{d\beta}{d\tau} \cdot \frac{c_2}{\alpha - \beta}; \quad w_2 = \frac{dc_3}{d\tau} - w_3, \tag{2}$$

where c_1, c_2, and c_3 are the concentrations of isopropyl alcohol, propylene, and propane in mM per liter of vapor (N.T.P.) of the initial alcohol, and α, β, and γ are the specific radioactivities as percentages of the initial propylene radioactivity.

EXPERIMENTAL

The decomposition of isopropyl alcohol over vanadium trioxide was studied at 315°C and different space velocities.* The study was carried out in a flow apparatus. A V_2O_5 catalyst was prepared as described in [6]. The V_2O_5 was reduced to the trioxide at 417°C for ten hours in a current of dry electrolytic hydrogen purified from oxygen impurities. A 6 ml portion of the catalyst was placed in the catalysis tube. Each portion was used for two experiments only. In the first (control) experiment the catalytic activity of the portion in question was determined in respect to the decomposition of isopropyl alcohol at 315°C and feed rate 0.15 ml/min, and then the experiment was carried out with the addition of labeled propylene. Experiments with additions of labeled propylene were carried out only on those portions of the catalyst which possessed approximately equal initial catalytic activity. The labeled propylene was obtained by dehydration of radioactive isopropyl alcohol over Al_2O_3 at 300°C. It was established chromatographically that this propylene was free from propane and other hydrocarbons. The specific activity of the original propylene amounted to 28950 cpm per mg of barium carbonate. The labeled propylene was diluted tenfold with hydrogen and supplied to the catalysis tube in amount 1.5 mole% of the raw alcohol. The propylene feed was controlled by a rheometer.

The composition of the liquid catalyzate was determined by the method of two-stage titrations of alcohol and acetone [6], by oxidimetry and against hydroxylamine respectively. The gaseous portion of the catalyzate was analyzed, and in the experiments with addition of labeled propylene it was also separated by chromatography. Special experiments with a synthetic mixture of propane and labeled propylene showed that these gases separate quantitatively. In order to determine the radioactivities, the obtained propane, propylene, and liquid portions of the catalyzate were burnt in a current of oxygen, the carbon dioxide which was produced was bubbled through baryta water, and targets were prepared as described earlier [7].

The concentrations of the reaction products, in mM per liter (N.T.P.) of original alcohol, are given in Table 1 for different contact times, τ. The value of τ was defined as the reciprocal of the space velocity.

The values of the specific radioactivities of the reaction products, as percentages of the radioactivity of the original labeled propylene, are given in Table 2.

From Table 2 all the evidence points to the fact that hydration of the propylene does not occur under the reaction conditions, since the liquid portion of the catalyzate is practically nonradioactive. The propane is also nonradioactive. It follows from this that the rates w'_1 and w_3 in Eq. (1) are practically equal to zero since $d\alpha/d\tau$, $d\gamma/d\tau$, and $(\gamma - \alpha)$ are close to zero.

Hence, the propane is formed by the process with rate w_2 in Eq. (2), and so propane forms through hydrogenolysis of isopropyl alcohol, and not through hydrogenation of propylene. Accordingly, of the two mechanisms considered in [6] in order to calculate the energies (Q) of the bonds between the reacting atoms and the catalyst surface, the second, in which the activation energy of isopropyl alcohol dehydration is determined from experimental data about the rate of formation of propylene, should be discarded (see above).

* Laboratory assistant E. M. Skyl'skaya participated in the experimental part of our work.

TABLE 1.

Material	Amount of product (mM/liter)		
	expt. 2 (τ = 4.3 sec)	expt. 1 (τ = 8 sec)	expt. 3 (τ = 22.2 sec)
iso-C_3H_7OH	27.4	22	15.3
CH_3COCH_3	7.5	9.2	13.3
C_3H_8	8.1	11.7	13.3
C_3H_4	1.7	1.8	3.1
Total (mM/liter) (in respect to carbon)	44.7	43.7	45.0
Total as % of original alcohol	100.0	98	100.8

TABLE 2.

Material	Sp. activity (% of initial activity)		
	expt. 2 (τ = 4.3 sec)	expt. 1 (τ = 8 sec)	expt. 3 (τ = 22.2 sec)
Liquid portion of the catalyzate	0.02	0.03	0.00
	(Practically nonactive)		
C_3H_8	0.4	0.07	0.00
	(Practically nonactive)		
C_3H_6	50.1	36.8	18.4

SUMMARY

1. The mechanism by which propane forms from isopropyl alcohol over vanadium trioxide was studied at 315°C with the use of propylene labeled with radiocarbon-14. Under these reaction conditions propane forms practically only through hydrogenolysis of isopropyl alcohol, and not through hydrogenation of propylene.

2. The rate of isopropyl alcohol dehydration is determined from the rate of formation of propylene.

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THE EFFECT OF ALKALI METAL OXIDES ON THE ACTIVITY, SELECTIVITY AND THE PHASE COMPOSITION OF BINARY CATALYSTS BASED ON Al_2O_3

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Translated from Izvestiya Akademi Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1552-1558, September, 1961
Original article submitted February 16, 1961

It is known that the addition of alkalis considerably alter the properties of catalysts. Thus, iron catalysts for the synthesis of ammonia, and alumina catalysts for the dehydrogenation of paraffins, contain K_2O as an essential component. However, this problem has still not been studied in sufficient detail and the published information available is possibly limited to the examples cited. It is therefore of interest to determine the effect of adding alkalis on the general and specific activity and selectivity of binary catalysts of different composition (based on aluminium oxide) taking part in parallel reactions and to determine the possible variation of the phase composition and texture.

EXPERIMENTAL

The following catalysts were obtained by co-precipitating the two oxides with ammonia and calcining at 400-450°: $NiO-Al_2O_3$, $Fe_2O_3-Al_2O_3$, $Cr_2O_3-Al_2O_3$, and $ZrO_2-Al_2O_3$. Following the results of the investigation on these catalysts carried out recently, [1-5], they were used in the present investigation. The oxides of the alkali metals were saturated with a solution of KNO_3 or $NaNO_3$ and heated at 600°, or in certain cases, at 400 and 1000°, for 6 hours. In Table 1, the letters represent the original catalysts and the numbers represent the catalysts with addition of alkali. The table gives the properties of the catalysts and the results of the activity. The activity was estimated by the pro-

TABLE 1. Degree of Conversion in the Dehydrogenation-Dehydration of Isopropyl Alcohol

Catalyst		Addition of alkali metal oxide, wt, %	Specific gravity	S m^2/g	Degree of conversion, % at					
					290°		320°		350°	
No.	Composition, mole %				C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2
A	$18Fe_2O_3$, $82Al_2O_3$	—	0,86	203	92	2,6	—	—	—	—
1	The same	Na_2O; 3,5	0,76	112	1,2	18	1,3	36	2,7	58
B	$40Fe_2O_3$, $60Al_2O_3$	—	0,9	146	91	4	—	—	—	—
2	The same	Na_2O; 3,0	0,93	104	1	18	1,3	35	1,3	50
C	$46Fe_2O_3$, $54Al_2O_3$	—	1,0	125	85	5	—	—	—	—
3	The same	K_2O; 2,0	1,0	151	2,7	21	4,2	41	8,4	64
4	The same*	K_2O; 4,0	1,12	120	0,8	11	3,2	34	6	54
D	$9NiO$, $91Al_2O_3$	—	0,87	198	100	—	—	—	—	—
5	The same	K_2O; 4,0	0,93	267	1,5	17	4,2	26	11	39
6	The same	Na_2O; 4,0	0,9	214	3	9	8	22	12	29
E	$20NiO$, $80Al_2O_3$	—	0,77	210	100	—	—	—	—	—
7	The same	K_2O; 3.0	0.8	162	0.7	19	2	28	6	47
F	$15Cr_2O_3$, $85Al_2O_3$	—	0,54	255	41	3	63	2	—	—
8	The same	K_2O; 3,0	0,76	210	3	18	6	25	15	42
G	$50Cr_2O_3$, $50Al_2O_3$	—	0,94	142	32	3	72	3	—	—
9	The same	K_2O, 2,0	1,2	120	3	22	7	36	11	38
H	ZrO_2	—	1,3	41	—	—	42	3	—	—
10	$15ZrO_2$, $95Al_2O_3$	K_2O; 3,0	0,7	175	—	—	17	4	39	7

* The catalyst was prepared by saturating Al and Fe hydroxides with a solution of KNO_3.

cedure described in our previous communications [3,5]. The activity was determined from the decomposition of absolute isopropyl alcohol over the range of temperatures 290-350°; C_3H_6 is used to designate the dehydration reaction and H_2 the dehydrogenation of alcohol. The experiments with alumino-chromia catalyst were carried out with a space velocity of 2.3 hr^{-1}. The space velocity used for the other catalysts was 1-1.5 hr^{-1}.

The values of the specific surface S of the catalysts were measured by the adsorption of benzene vapors at 20°C in a vacuum apparatus. The experimental results were calculated by the method of Brunauer, Emmett and Teller (BET). The variation in the porous structure was not determined directly but estimated approximately from the variation of the specific gravity of the catalysts (on a moisture free basis). Since the A-3 catalysts already caused an intensive decomposition of the alcohol at low temperatures, it was decided not to carry out the experiments at high temperatures.

The phase analysis was carried out using x-ray diffraction photographs obtained with a RKD camera (diameter d of the camera, 57.3mm) by the asymmetric method of radiation with filtered CuK_α and FeK_α. As was shown earlier [1] NiO does not exist as a separate phase in nickel oxide-alumina catalysts with NiO < 40-50 mole % and these catalysts represent single phase systems consisting of solid solution components. No new phases were observed after the addition of K_2O. This is not the case with ZrO_2 catalysts. It was shown earlier [2] that ZrO_2-Al_2O_3 catalysts give the following phases: heating at 600°, γ-Al_2O_3 only is formed and at 750°C, γ-Al_2O_3 and tetragonal ZrO_2. After introducing K_2O into the catalyst the phase composition altered: The x-ray diffraction pattern showed lines of a monoclinic modification of ZrO_2 (or potassium zirconate), and these lines became more intense after the catalyst had been used in the decomposition of isopropyl alcohol.

Only γ-Al_2O_3 was found on the x-ray diffraction pattern of the alumino-chromia catalyst C, but with catalyst D (50% Cr_2O_3) α-Cr_2O_3 and only traces of γ-Al_2O_3 were found. However, the x-ray diffraction of catalyst 9, obtained after adding K_2O to D, showed that not only was α-Cr_2O_3 present but there were clear indications of the presence of γ-Al_2O_3 which is obviously explained by the effect of the alkali metal oxide because under these same temperature conditions, but without alkali, γ-Al_2O_3 is not formed.

Ferro-alumina gels B and C, calcined at 400°C only contained one crystalline phase: γ-Al_2O_3, and after calcining at 600 and 750°C, two phases: γ-Al_2O_3 and α-Fe_2O_3. Both these phases represent respectively solid solutions of ferric oxide in aluminium oxide (spinel lattice) and aluminium oxide in ferric oxide (corundum lattice). After the catalysts have been used at temperatures not higher than 600°C for the decomposition of isopropyl alcohol, the Fe_3O_4 phase is formed because ferric oxide is reduced to Fe_3O_4. The introduction of K_2O or Na_2O into the catalyst alters the phase composition and leads to the appearance of cubic ferric oxide, γ-Fe_2O_3. This occurs in catalysts 3 and 4; γ-Fe_2O_3 was identified on the x-ray diffraction pattern from published tables [6]. The catalyst 4, as well as containing γ-Al_2O_3 and γ-Fe_2O_3, also contained α-Fe_2O_3. The analogous effect—the formation of γ-Fe_2O_3—was also found by adding KNO_3 to the jointly precipitated oxides after calcining them at 600°C.

RESULTS

The experiments carried out to determine the effect of adding alkalis on the activity and selectivity of binary catalysts based on Al_2O_3 gave a well defined picture of the variation of these properties. As can be seen from the results of Table 1 the total degree of conversion in the decomposition of isopropyl alcohol in every case where alkalis are added, considerably decreases: with ferro-alumina and nickel-alumina catalysts by 4-5 times, with alumino-chromia and alumino-zirconia catalysts approximately twice. These large variations in the total activity cannot be explained by a variation of the texture of the catalysts: although in the majority of cases, the introduction of alkali additives by the method described also leads to a decrease of the value of specific surface S it does not alter in proportion to the variation of the activity. Moreover, there are cases (catalysts 5 and 6) when S increases with the addition of alkali but these show a considerable decrease of activity. The specific gravity (on a moisture free basis) of the catalysts increases slightly which obviously is due to a decrease of the porosity and a change of its character. From the results in Table 1 it is obvious that with addition of alkali there is a decrease in total activity of the catalysts due to the suppression of the dehydrating activity of the catalysts. The total degree of conversion rapidly rises with the temperature at which the alcohol is decomposed. But from the results of Table 1 it is obvious that the increase in the dehydrogenating activity by far exceeds the increase in dehydrating activity. Table 1 also shows that at first the degree of conversion (with addition of 2-4 % of alkali to the given catalyst), alters approximately to the same extent and secondly, that K_2O acts rather more strongly than Na_2O which is most easily seen from the results obtained with catalysts 5 and 6.

Since the variation in the properties of catalysts of different composition and texture were studied it was important to compare their specific activity (A_{sp}) for each of the reactions. The values of A_{sp} calculated from the experimental data are the same as those from the earlier investigations [3, 5] ($A_{sp} = k/S$, where k is the reaction rate constant). The results are given in Table 2, which in general, reproduce the variation in the total activity and the activity in the separate reactions which were observed from Table 1, although in Table 2 the effect of the magnitude of the surface and the rate (expressed in Mole/ min/ m^2) are excluded: the total magnitude of the specific activity A_{sp} rapidly decreases under the effect of the additive.

TABLE 2.

The Specific Activity of the Catalysts. The Values of $A_{sp} \cdot 10^6$ in Mole/min/m^2 obtained.

Catalysts		Specific activity at the temperature of decomposition					
No.	Composition, mole %	290		320		350	
		C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2
A	$18Fe_2O_3$—$82Al_2O_3$	2,12	0,05	—	—	—	—
1	same + Na_2O; 3,5%	0,04	0,66	0,05	1,3	0,09	2,10
B	$40Fe_2O_3$ — $60Al_2O_3$	2,8	0,11	—	—	—	—
2	same + Na_2O_3; 3,0%	0,03	0,62	0,04	1,2	0,04	1,74
C	$46Fe_2O_3$ — $54Al_2O_3$	2,6	0,15	—	—	—	—
3	same + K_2O; 2,0%	0,06	0,47	0,09	0,89	0,18	1,42
4	same + K_2O; 4,0%	0,02	0,28	0,01	0,86	0,13	1,36
D	$9NiO$ — $91Al_2O_3$	—	0	—	—	—	—
5	same + K_2O; 4,0%	0,02	0,25	0,06	0,35	0,15	0,53
6	same + Na_2O; 4,0%	0,04	0,16	0,13	0,38	0,21	0,51
E	$20NiO$ — $80Al_2O_3$	—	0	—	—	—	—
7	same + K_2O; 3,0%	0,02	0,48	0,04	0,72	0,15	1,20
F	$15Cr_2O_3$ — $85Al_2O_3$	1,48	0,09	2,3	0,05	—	—
8	same + K_2O; 3,0%	0,10	0,59	0,19	0,82	0,50	1,37
G	$50Cr_2O_3$ — $50Al_2O_3$	1,2	0,12	2,7	0,1	—	—
9	same + K_2O; 2,0%	0,09	0,83	0,03	1,36	0,42	1,44
H	ZrO_2	—	—	2,0	0,09	—	—
10	$15ZrO_2$—$85Al_2O_3$+K_2O; 3,0%	—	—	0,46	0,11	1,05	0,19

The second consequence of adding alkali to the Al_2O_3 based catalysts, and the most important, is the extremely rapid variation of the selectivity effects: apart from the suppression of dehydration already referred to above, there is an intense rise in the dehydrogenation activity, and even when dehydrogenation activity has been absent (catalysts 5-7) to start with, the dehydrogenation activity appears. The properties and magnitude of these variations in the selectivity of the catalysts are given in Table 3, in which the values of the selectivity coefficients are given in the form $k_s = A_{H_2} / (A_{H_2} + A_{C_3H_6})$. Therefore $k_s = 0$ corresponds to 100% dehydrogenation.

TABLE 3.

Variation in the Selectivity of the Catalysts under the effect of Alkali Additives

Catalyst		Decomposition temp. of alcohol			Catalyst		Decomposition temp. of alcohol		
No.	Composition	290	320	350	No.	Composition	290	320	350
A	Fe_2O_3 — Al_2O_3	0,03	—	—	D	NiO — Al_2O_3	0	—	—
1		0,94	0,96	0,96	5		0,92	0,86	0,67
B		0,04	—	—	6		0,75	0,73	0,70
2		0.95	0,96	0,97	E		0	—	—
C		0,06	—	—	7		0,96	0,93	0,89
3		0,88	0,90	0,88	F	Cr_2O_3 — Al_2O_2	0,06	0,03	—
4		0,93	0,91	0,90	8		0,86	0,81	0,74
3	ZrO_2 — Al_2O_3	—	0,07	—	G		0,09	0,04	—
10		—	0,19	0,15	9		0,88	0,84	0,77

The calculation of k_s from the degree of conversion gives a result very close to that calculated from A_{sp}. In the range of temperatures investigated the selectivity of ferro-aluminium catalysts hardly alters but in the other catalysts k_s slightly decreases with an increase of temperature of the tests.

In analysing how the activity and selectivity of the catalysts vary with addition of alkali it is necessary in the first place to consider the following causes: the variation of the chemical composition of the surface, the variation of the phase composition, and the variation of the electron properties. The basic factor due to the method of introducing the additive to the catalyst, must be the variation of the chemical composition of the surface which may lead both to the formation of surface compounds due to the components of the catalyst combining with the additives (formation of aluminate, chromite, zirconate) and also to the fact that on the crystal surfaced, e.g.,of NiO or Fe_2O_3, free alkali is retained to a greater or lesser degree. To confirm these points experimentally we carried out supplementary tests with some catalysts with space velocities of 2.3-2.7 hr^{-1}, theresults of which are given in Table 4. With 3% K_2O added to Al_2O_3 (partial formation of aluminate) the activity at 350 is lower and at 450°C higher, than the activity of Al_2O_3 without an additive whereas at 450°C the dehydrogenation activity, absent at lower temperatures, appears. However, in addition, the dehydration activity also increases. Crystalline potassium aluminate in which the ratio of K_2O to Al_2O_3 is stoichiometric, also catalyses the decomposition of the alcohol in both directions although it produces a smaller degree of conversion than the preceding catalyst, probably because of the smaller value of the specific surface. An experiment on the catalytic activity of powdered KOH contained in a glass fiber bag showed that despite the very small specific surface it has a most pronounced catalytic activity. The application of 20% KOH showed that an extremely active catalysts is obtained in this way which acts on isopropyl alcohol very differently from the way the underlayer of activated carbon acts.

TABLE 4.
Supplementary Tests

Catalyst	Amt. g	Specific surface m^2/g	T.°C decomp of alcohol	Activity		Degree of conversion		Specific activity	
				C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2
Al_2O_3	1,5	175	350	74	0	22	0	0,83	0
$97Al_2O_3 + 3K_2O$	1,5	300	350	33	0	1	0	0,4	0
$97Al_2O_3 + 3K_2O$	1,5	300	450	128	105	43	35	1,56	1,3
Potassium aluminate	—	—	400	—	—	5		—	—
Same	—	—	450	33	58	11	18	—	—
KOH, powder	—	<1	450	6	37	2	12	2	12
20% KOH on activated carbon	0,5	70	350	2,0	150	0,6	51,5	0,02	15
Activated carbon	0,5	140	350	24,6	11,6	8,4	4,0	1,2	0,6

Note: The activity is given in ml of gas for 1 ml of alcohol; the specific activity in Mole/ m^2/ min·10^6.

We take the opportunity to note here that the experiments permitted us to find the natural catalytic activity with respect to the decomposition of the alcohols with a) activated carbon, b) KOH and c) potassium aluminate. As far as we know none of these three has been tried as a heterogeneous catalyst for similar reactions up to the present time. The catalysts given in the Table 4 are divided up by selectivity in the following way: completely dehydrating (k_i =O) catalysts: Al_2O_3 and Al_2O_3 + KOH at 350°C; preferentially dehydrating: Al_2O_3 + KOH at 450°C, k = 0.47, and activated carbon k_i = 0.3; preferentially dehydrogenating: potassium aluminate with k_i = 0.6 and KOH with k_i = 0.85; and finally a completely dehydrogenating catalyst: 20% KOH on carbon. The value of k_i shows that the dehydrogenating activity increases with an increase of the concentration of KOH in the catalyst. Therefore, the comparison of the results given above with the results from the selectivity of the catalysts of the main series (Table 3) shows that in the latter, excluding the content of ZrO_2, the selectivty proves to be intermediate between this type of potassium aluminate and KOH, while in a number of cases, it is closer to the latter. In our preceding work it was shown that Fe_2O_3-Al_2O_3 catalysts are preferentially dehydrating [5] but NiO-Al_2O_3 catalysts with a content of less than 30% mole are solely dehydrating. Therefore the selectivity data obtained in the present investigation permits us to consider that there are aluminates and free alkali on the surface of three component catalysts. The hydrolytic decomposition of the aluminate and the compounds similar to it, with water formed during the dehydration of alcohol.

It is not possible to confirm that all the additive is concentrated on the surface of the catalyst. The fact that part of it changes in the crystal spaces is known from the x-ray results which is evidence that the phase structure of the catalysts vary and that certain phases are stabilized. These results are discussed below. However, the effect of the variation of the phase composition in this case, does not lead to a quantitative estimation because of the pronounced influence of the surface composition and it may be considered secondary. The rapid penetration of the additive (ions of K, Na, OH) inside the crystals must act on the electron mechanism so that additional electron levels are formed. If we consider the results we have obtained from the viewpoint of the electron theory, then it is necessary to bear in mind that according to Vol'kenshtein [7] and Garner [8] the dehydrogenation reaction of alcohols proceeds by an acceptor mechanism, and the parallel reaction of dehydration proceeds by a donor mechanism. Thus, our results show that KOH and NaOH intensify the acceptor type reaction and suppresses the donor type reaction. As a consequence of the fact that an increase of the Fermi level [7] corresponds to an intensification of the acceptor reaction (dehydrogenation), it follows that in the cases which we investigated the additives played the role of donor additives.

Passing over to the effect of the additives KOH and NaOH on the phase composition of the catalysts let us note that x-ray analysis showed that in the presence of the amorphous phase or of components able to form polymorphous varieties such additives may lead to a variation in the phase composition. Thus, in the first place, they facilitate the crystallization of the amorphous phase. This is clear from the fact, for example, that in catalyst 10 a monoclinic phase of ZrO_2 or potassium zirconate is already formed when the catalyst is calcined at 600°C, whereas in the presence of γ-Al_2O_3 in the same catalyst without alkali, the ZrO_2 is found to be in the amorphous state [2]. Even if the monoclinic phase is considered as potassium zirconate then, in this case, it is also clear that the additive leads to the crystallization of the amorphous phase and probably to the variation of the distribution of ZrO_2 in γ-Al_2O_3, since the bulk crystalline phase of zirconate is formed.

The role of the additives referred to above, in the phase transformation where the components are able to produce polymorphic allotropic forms, may be brought out from our results with catalysts containing ferric oxide or chromium oxide. Thus, in the case of alumino-chromia catalysts (e.g.,9) if an alkali metal oxide is added then even at 600°C the crystallization of γ-Al_2O_3 occurs, which in catalyst E (without alkali) does not occur up to 1000°C. Hence, it is also possible to conclude that the addition of KOH stabilizes the spinel lattice of γ-Al_2O_3. Both these results are completely applicable even for ferro-alumina gel catalysts when the phase transformation and stabilization of the spinel lattice are also present. The addition of KOH causes crystallization to amorphous ferric oxide [4] where it is in the form of γ-Fe_2O_3, having the spinel lattice but not the corundum phase of α-Fe_2O_3, as this occurs in the absence of KOH additive but at a higher temperature of (cf. [4]). In addition let us note the following. The compounds γ-Fe_2O_3 and Fe_3O_4 have parameters respectively of 8.33 and 8.37 Å [9]. As a consequence, the powder diffraction pattern of these oxides are similar [6] which hinders a well defined interpretation of the x-ray pattern and requires additional data. In work carried out earlier [4] the cubic phase of ferric oxide only appeared in used catalysts i.e. after their residence in a reducing atmosphere at high temperatures. The effect of the alcohol vapors and hydrogen on Fe_2O_3 was to reduce it to Fe_3O_4. It is necessary to remember that this phase is absent in catalysts which have not been used. In the present work the cubic modification of ferric oxide appeared in the catalysts which had not been subjected to the action of a reducing agent. Consequently, Fe_3O_4 cannot be formed because it is only formed as a result of the dissociation of Fe_2O_3 at temperatures above 1200-1300°C, and at lower temperatures the reverse process occurs where Fe_3O_4 is oxidized into Fe_2O_3 [10].

At the present time it is possible to consider as an established fact that γ-Al_2O_3, γ-Fe_2O_3 and γ-Cr_2O_3 exist only in the presence of stabilizing additives. For example, Glemser and Rieck [11] verified that γ-Al_2O_3 always contains water in its lattice in the form of hydroxyl ions; Davis et al. [12] found that chromium oxide is formed with a deformed cubic lattice in the presence of γ-Al_2O_3. From the data of Emmett and Love [13], γ-Al_2O_3 and ions of alkali metals have a stabilizing effect on γ-Fe_2O_3. The stabilizing effect of γ-Al_2O_3 on γ-Fe_2O_3 was also shown by de-Boer and Selwood[14], but Davis and Welch [15] established that γ-Fe_2O_3 cannot be formed in the complete absence of water. Thus, the results obtained by us agree very well with the published results with respect to the stability of γ-Fe_2O_3. As concerns the NiO-Al_2O_3 catalysts which we investigated then this is the most simple case: the appearance of the NiO phase in them even when the content of this component is not more than 20% in the catalysts is explained by the decomposition of the solid solution or that of the spinel $NiAl_2O_4$, by the action of the alkali.

SUMMARY

1. The variation of the general and specific activity and selectivity of NiO-Al_2O_3-, Fe_2O_3-Al_2O_3-, Cr_2O_3-Al_2O_3-, and ZrO_2-Al_2O_3-catalysts in the decomposition reaction of absolute isopropyl alcohol was determined at 290-350°C.

The phase composition and values of the specific surface with the addition of 2-4% of K_2O and Na_2O were also obtained.

2. These additives have the following effects: they reduce the general activity of the catalysts considerably due to the suppression of the dehydrating activity; they rapidly alter the selectivity of the catalysts due to the increase or the emergence of dehydrogenating activity; facilitates the crystallization of amorphous phases in the catalysts; stabilizes the γ-modification of the oxides of Fe and Al i.e.,of a spinel type lattice, and in the case of polymorphous components of the catalyst may change the character of the crystallization i.e.,lead to a phase transformation.

3. The natural catalytic activity with heterogeneous decomposition of isopropyl alcohol has been obtained: a) with activated carbon, b) with potassium aluminate and c) with KOH.

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INVESTIGATION INTO THE PHYSICAL AND CHEMICAL PROPERTIES OF WS_2-CATALYSTS

COMMUNICATION 7. HYDROGENATION OF PHENOL UNDER PRESSURE IN THE PRESENCE OF A NONMIXED WS_2-CATALYST PROMOTED BY SULFUR, SELENIUM, TELLURIUM OR PHOSPHORUS

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1559-1561, September, 1961
Original article submitted January 13, 1961

In the preceding paper [1] in a detailed study of the effect of sulfur on the activity of a nonmixed WS_2-catalyst it was established that promoting the catalyst by sulfur not only enhances its activity but also markedly changes its selectivity in the direction of an intensified ability to hydrogenate. Because of the great interest, in particular for the industrial applications, which highly selective catalysts for the hydrogenation of aromatic hydrocarbonds have acquired nowadays, we have examined and compared in the present study the effect exerted on the activity and selectivity of a nonmixed WS_2-catalyst by sulfur, selenium and tellurium, which are located in one subgroup of Mendeleev's periodic system, and also that exerted by phosphorus. In this the activity of the WS_2-catalyst was tested, similarly as was done in the paper [1], in the hydrogenation of phenol in an autoclave at 380°C and an initial H_2 pressure equal to 110 atm.

EXPERIMENTAL

For investigating the activity we took two WS_2-catalysts which had not been in operation nor had undergone any treatment: sample 3 having an excess of sulfur (atomic ratio S : W = 2.30) and sample 4 having an excess of tungsten (S : W = 1.92). We have already studied previously these catalysts in the papers [1-3]. Moreover, we have tested the sample 3 (H_2) with S : W = 1.88, which was prepared by a thermal treatment of sample 3 at 400°C in a current of hydrogen under a pressure 100-120 atm during ten hours.

The hydrogenation of phenol was carried out at 380° during one hour in a rotating autoclave of 0.5 liter capacity, while we used a standard manometer with 2 atm scale divisions, which enabled us to determine the pressure with an accuracy of ± 0.2 atm. The hydrogenation procedure and the analysis of the reaction products were completely similar to those used in the paper [1]. All experiments were done under strictly identical conditions. Into the autoclave we poured 30 g phenol which had been distilled before and 1 g catalyst ground to a fine powder. In order to promote the catalyst we used stick sulfur (0.041 g), gray crystalline selenium (0.099 g), spectrally pure tellurium (0.160 g) or red phosphorus (0.039 g), which all had been ground to fine powders, whereas the promoter was carefully mixed with the catalyst before it was poured into the autoclave. The results of the hydrogenation are given in the table. It must be noted that, when compared with paper [1], in the present study on the catalyst 3 somewhat more and on the catalyst 4 less hydrogen and phenol have reacted, whereas these differences are markedly greater than the deviations between parallel experiments in both studies. Since in the present study and that of paper [1] the hydrogenation of phenol was carried out under completely identical conditions and the catalyst samples were taken from one and the same portion, which was kept in a nitrogen atmosphere, we have to draw the conclusion that under such conditions of storage the activity of a nonmixed WS_2-catalyst changes with time *. At the same time it must be stressed that by admixture of sulfur the activity and the selectivity of the catalysts in the present study changed in the same way as was found in the paper [1] and, therefore, the data obtained in the present investigation are quite suitable for examining the effect of promotors on the properties of a WS_2-catalyst.

* The present study was carried out $1\frac{1}{2}$ years after the investigation reported in [1].

As the table points out, amounts of selenium, tellurium or phosphorus which are small in comparison to the amount of catalyst markedly change the activity and selectivity. In order to compare the promoting properties all elements studied were applied in an equiatomic amount (~1.25 10^{-3} g-at) so that an identical number of promoter atoms participated in the reaction.

Hydrogenation of Phenol under Pressure on a Promoted Nonmixed WS_2-Catalyst

Catalyst	Amt of phenol Φ, g		H_2 pressure, atm			$\Delta H_2/\Delta\Phi$ $MH_2/M\Phi$
	non-reacted	reacted	original	after the experiment	consumed in the reaction	
3	2,9	27,1	111,6	78,4	33,2	2,40
3	1,8	28,2	112,4	80,0	32,4	2,24
3 + Se	6,2	23,8	112,4	75,0	37,4	3,08
3 + Te	21,5	8,5	112,8	103,0	9,8	2,25
3(H_2)	18,2	11,8	112,6	104,6	8,0	1,33
3(H_2) + Se	20,1	9,9	112,8	100,0	12,8	2,53
4	11,3	18,7	112,2	96,4	15,8	1,65
4	11,5	18,5	107,8	92,4	15,4	1,63
4 + S	5,2	24,8	111,8	88,8	23,0	1,81
4 + Se	13,6	16,4	110,6	90,0	20,6	2,46
4 + Te	24,4	5,6	110,8	107,0	3,8	1,33
4 + P	17,9	12,1	112,6	100,0	12,6	2,04

Our experiments proved that selenium, just as sulfur, raises the amount of hydrogen entering into reaction. However, unlike sulfur, which also raises the amount of reacted phenol, selenium decreases the amount of phenol consumed in the reaction. The selectivity of the catalyst changes in such a way that by promoting with selenium its ability to hydrogenate is raised more highly above the activity of the nonpromoted one than is done by promoting with sulfur. This is particularly clearly manifested, if as a definition of the hydrogenation ability of the catalyst we use, as was provisorily done in the paper [1], the molar ratio $\Delta H_2/\Delta\phi$, which in the table is given for each experiment. Phosphorus and especially tellurium sharply decrease the consumption of hydrogen and phenol in the reaction. Meanwhile phosphorus causes a certain increase and tellurium a decrease in the hydrogenation ability of a WS_2-catalyst. It must be noticed that the character of the promoting effect of selenium and tellurium does not depend on the S:W ratio in the catalyst, as is evident, when sample 3 having an excess of sulfur is compared with samples 4 and 3 (H_2), which have an excess of tungsten.

Because in the present study it has been established that selenium has a much higher promoting effect on the hydrogenation ability of a WS_2-catalyst than does sulfur, it may be assumed that at an equal surface area the hydrogenation activity of tungsten selenide WSe_2 should be higher than that of a WS_2-catalyst. This assumption is made still more interesting by the fact that tungsten selenide WSe_2 has a laminated crystal structure quite analogous to that of WS_2 with nearly the same values of the lattice parameters [4] and, consequently, WSe_2, just as WS_2, may be obtained in the form of a compound with a high specific surface area.

SUMMARY

1. The effect of equiatomic amounts of sulfur, selenium, tellurium or phosphorus on the activity of a nonmixed WS_2-catalyst in the hydrogenation of phenol under pressure has been compared.

2. When compared with sulfur, promoting by selenium more strongly changes the selectivity of the catalyst in the direction of an enhanced hydrogenation ability.

3. Tellurium and phosphorus lower the activity; meanwhile tellurium somewhat decreases and phosphorus increases the hydrogenation ability of a WS_2-catalyst.

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ISOTOPEC EXCHANGE STUDY OF ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

COMMUNICATION 4. KINITICS OF THE ISOTOPE EXCHANGE OF THE ETHYL ESTER OF α-BROMMERCURY PHENYLACETIC ACID WITH MERCURIC BROMIDE LABELED WITH Hg^{203}, IN DIMETHYLFORMAMID

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1561-1565, September, 1961
Original article submitted January 26, 1961

In line with the systematic investigation of the isotope exchange reaction of the type $R\text{-}HgX + Hg^{*} X_2 \rightleftharpoons R\text{-}Hg^{*}X + HgX_2$, we have already in Ref. [1-3] studied the kinetics of the isotope exchange of the ethyl ester of α-brommercury phenylacetic acid with mercuric bromide pyridine aqueous dioxane. The present paper describes the results of the study of the kinetics of the reaction of the ethyl ester of α- brommercury phenylacetic acid with mercuric bromide, labelled with the radioactive isotope Hg^{203}

$$C_6H_5CH(HgBr)COOC_2H_5 + Hg^{*}Br_2 \rightleftarrows C_6H_5CH(Hg^{*}Br)COOC_2H_5 + HgBr_2$$

in dimethylformamid (DMF).

EXPERIMENTAL

The reaction kinetics was studied by the previously described method of paper radiochromatography, Ref. [4]. The concentration of the reagents was varied over the range 0.01–0.04 mol/liter. Table 1 gives the experimental data on the isotope exchange rate at 70°C for $C_{HgBr_2} = C_{Hg\text{-ester}} = 0.03$ moles/liter.

From the graph constructed from this data (Fig. 1 curve 1), it is clear that the value of - log (1-F) is not a linear function of time, but the dependence is described by a curve of autocatalytic type. The cause of this phenomenon is apparently to be found in the fact that under our conditions a mercuro-organic salt reacts both with the mercuric bromide and with the complex of mercuric bromide and dimethylformamid, in which the second reaction goes considerably faster, and determines the kinetics of isotope exchange along with the process of complex formation. Thus the overall isotope exchange process may be represented by the following scheme:

$$R\text{–}HgBr + Hg^{*}Br_2 \rightleftharpoons R\text{–}Hg^{*}Br + HgBr_2 \quad (1)$$

$$Hg^{*}Br_2 + n\ DMF \rightleftharpoons Hg^{*}Br^{*} \cdot n\ DMF \quad (2)$$

$$R\text{–}HgBr + Hg^{*}Br_2 \cdot n\,DMF \rightleftharpoons R\text{–}Hg^{*}Br + HgBr_2 \cdot n\,DMF \quad (3)$$

TABLE 1.
Isotope Exchange in Dimethylformamid Without Preliminary Heating

t, min	A_{HgBr_2}, counts/min	$A_{Hg\text{-ester}}$ counts/min	F, %	t, min	A_{HgBr_2}, counts/min	$A_{Hg\text{-ester}}$ counts/min	F, %
60	2058	22	2,1	300	2200	350	27,5
120	2835	137	9,2	410	1923	511	42,0
160	1904	114	11,3	480	2120	721	50,8
240	1626	203	22,2	530	2091	790	54,8

The second reaction is practically irreversible, and from the mutual position of curves 1 and 2 in Fig. 1 it is clearly evident that the rate of reaction 1 is very small in comparison with the rate of reaction 3.

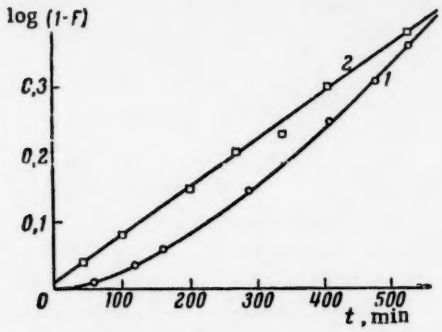


Fig. 1. Kinetics of the isotope exchange of $C_5H_5CH(HgBr)COOC_2H_5$ with Hg^*Br_2 at 70°C in DMF; c = 0.03 mol/liter; Curve 1—without preliminary heating, 2—with preliminary heating of the Hg^*Br_2 solution in DMF for five hours.

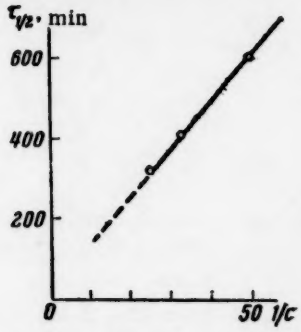


Fig. 2. Half exchange period as a function of reciprocal concentration.

To test this assumption the solution of mercuric bromide in DMF was kept for a long period of time at elevated temperature (five hours at 70°C) before the reaction and then was mixed with the solution of the mercuro organic compound. This gave a good linear curve of - log (1-F) against t (Fig. 1, curve 2), which confirms the assumption made. Table 2 gives the kinetic data on the isotope exchange with equimolecular concentration of 70°C. To determine the order of the reaction a curve was constructed giving the half exchange period as a function of the reciprocal concentration (Fig. 2). The resolving straight line shows that the overall reaction is second order.

To determine the reactivation energy the reaction rate was measured at different temperatures. The data are given in Table 3. Fig. 3 gives the curves of -log (1-F) equal to f (t) for different temperatures, thus, illustrating the change in the rate constants at different temperatures. This curve was used to find the values of the half exchange periods and the constants. Table 4 gives $\tau_{1/2}$, K_2, their logarithms, the absolute temperatures, and their reciprocals.

The constants in the Arrhenius equation were determined graphically (Fig. 4, curve a). The activation energy is E = 16.1 kcal/mol, log A = 8.7. The activation entropy, $\Delta S = -19.0$ entropy units at 60°C.

Kinetically the isotope exchange with the mercuric bromide -DMF complex is entirely similar to the exchange in pyridine. The reaction is also bimolecular, and the activation energy has the same value. The straight line b of Fig. 4 gives the data on pyridine for comparison. Both lines are parallel. This shows that in pyridine the mercuric bromide also reacts not as a free unionized molecule, but in the form of a complex. However, in this case the formation proceeds very rapidly because of the large nucleophilic property of the pyridine. It is possible to capture the complex formation stages in the more weakly nucleophilic that is in a more nuclear philic solvent like DMF. The complex forming properties of DMF have been described previously in Ref [5] and [6] *.

In our previous work, Ref. [1, 8, and 9], we have repeatedly observed the accelerating influence of organic bases on isotope exchange reactions of the type being described. One was inclined to think that the effect depends either on the complex forming properties of the base, or on the increased polarity of the solvents as a result of adding the polar molecules of the bases. The results of the present work definitely show the dominant role of complex

*A very interesting catalytic effect of DMF as well as pyridine was observed recently Ref. [7] in the synthesis of mercuro-organic compounds by the amalagam method.

formation. In addition it follows from these results that the complexes of the mercury halide with pyridine or DMF are stronger electrophlic reagents than the mercury halide molecules. This is not surprising, since the mercury halide molecules are covalent and nonpolar or only slightly polar. The complexes, on the other hand, are strongly polar, for example:

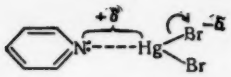


TABLE 2.
Kinetics of the Isotope Exchange of $C_6H_5CH(HgBr)\ COOC_2H_5$ with $Hg^*\ Br_2$ in DMF at 70°C and Equimolecular Concentrations

$c_{HgBr_2} = c_{Hg\text{-ester}}$	t, min	A_{HgBr_2}, counts/min	$A_{Hg\text{-ester}}$, counts/min	F, %	$\tau_{1/2}$, min	$K_2 \cdot 10^2$ liters/mol · min
0,02	40	1569	48	5,9		
	90	1507	94	11,8		
	180	1600	175	19,7		
	270	1507	230	26,5		
					600	2,89
	350	1002	201	33,4		
	420	1624	402	39,6		
	520	1197	354	45,7		
0,03	40	1756	86	9,3		
	100	1302	114	16,1		
	200	1575	279	30,1		
	270	1328	294	36,3		
					410	2,82
	340	1616	432	42,2		
	410	1510	502	50,0		
	530	1361	544	57,1		
		1522	665	60,8		
0,04	30	1315	46	6,8		
	70	1794	160	16,4		
	110	1856	251	23,8		
	140	1808	292	27,8		
	220	1854	456	39,5		
					310	2,79
		1958	434	36,3		
	270	1389	385	43,4		
	320	1625	568	51,8		
	380	2059	758	53,9		
		2054	811	56,6		

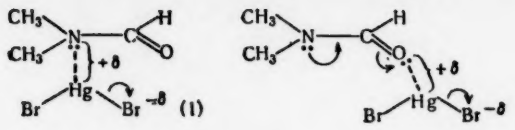
TABLE 3.
Kinetics of the Isotope Exchange of $C_6H_5\ CH(HgBr)\ COOC_2H_5$ with Hg^*Br_2 at Different Temperatures

$c_{HgBr_2} = c_{Hg\text{-ester}}$ mol/liter	t, °C	t, min	A_{HgBr_2}, counts/min	$A_{Hg\text{-esters}}$ counts/min	F, %	$\tau_{1/2}$, min	$K_2 \cdot 10^2$ liters/mol · min
0,03	60	60	1769	71	7,7		
		120	1743	113	12,2		
		240	1878	216	20,6		
						820	1,41
		330	1765	270	26,6		
		410	1726	311	30,6		
		450	1936	383	33,0		
0,03	70	40	1756	86	9,3		
		100	1302	114	16,1		
		200	1575	279	30,1		
						410	2,82
		270	1328	294	36,3		
		340	1616	432	42,2		
		410	1510	502	50,0		
		530	1361	544	57,1		
			1522	665	60,8		
0,03	80	30	1527	78	9,7		
		100	1627	251	26,7		
		140	1393	284	33,9		
		180	1453	366	40,2		
						235	4,92
		220	1550	476	47,0		
		250	1521	527	51,8		
		280	1413	535	55,0		

TABLE 4. Change in Half Exchange Period and Rate Constant with Temperature

T°, K	$1/T \cdot 10^4$, deg^{-1}	$\tau_{1/2}$, min	K_2, 1/M · min	log K_2
333	30,0	820	$1,41 \cdot 10^{-2}$	2,15
343	29,2	410	$2,82 \cdot 10^{-2}$	2,45
353	28,3	235	$4,92 \cdot 10^{-2}$	2,69

The question of the structure of the complex molecule formed between a mercuryhalide and DMF remains open, since generally speaking complex formation may occur either with a nitrogen atom (I) or with an oxygen atom (II). For complexes with iodine and acids the literature gives data in favor of the type (II) structure, Ref. [6,10].



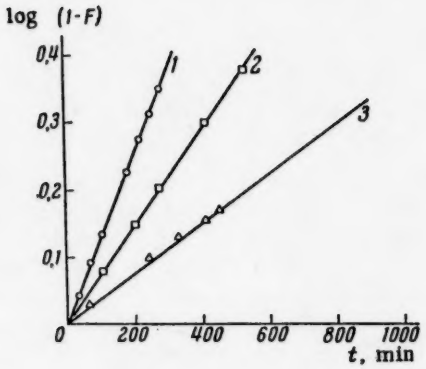


Fig. 3. Kinetics of isotope exchange in DMF at different temperatures: 1) 80°C; 2) 70°C; 3) 60°C; c = 0.03 mols/liter.

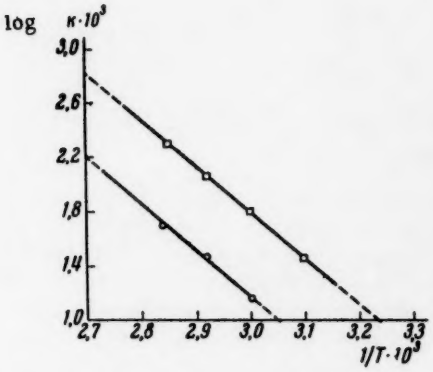


Fig. 4. Graph for determining the activation energy of the isotope exchange reaction of $C_6H_5CH(HgBr)COOC_2H_5$ with Hg^*Br_2 in DMF (straight line a) and in pyridine (straight line b).

SUMMARY

1. A study has been made of the kinetics of the isotope exchange of the ethyl ester of α-brommercuryphenylacetic acid with Hg^*Br_2 in DMF. It has been shown that the reaction proceeds with preliminary formation of the complex Hg^*Br_2 n DMF.

2. The overall order of the reaction with these complexes, namely the second order, has been determined along with the constants in the Arrhenius equation.

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RATE CONSTANT AND MECHANISM OF THE REACTION OF ATOMIC OXYGEN WITH 1, 2-DICHLORETHANE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1565-1571, September, 1961
Original article submitted March 25, 1961

In the literature there is information [1] concerning the reaction of atomic oxygen with chlorinated methanes: CCl_4, CHC_{13}, CH_2Cl_2 and CH_3Cl.

On the basis of the reaction products Harteck and Kopsch [1] concluded that in these reactions substitution of a single molecule: HCl or H_2 or Cl_2 by an oxygen atom occurs. There is also our experimental study on the reaction of atomic oxygen with ethane [2]. In this case it was found that an oxygen atom reacted with the ethane with cleavage of the ethane molecule at the C–C bond, with formation of a molecule of formaldehyde. In studying the reaction of atomic oxygen with dichlorethane it is of interest to ascertain whether the dichlorethane will react without cleavage of the C–C bond, or whether the reaction will occur with cleavage of the molecule at the C–C bond, with formation of a molecule of formaldehyde. In studying the reaction of atomic oxygen with dichlorethane it is of interest to ascertain whether the dichlorethane will react without cleavage of the C–C bond, or whether the reaction will occur with cleavage of the molecule at the C–C bond. The object of the present work therefore was to study the mechanism of the interaction of atomic oxygen with dichlorethane and the variation of the rate constant of the reaction of atomic oxygen with dichlorethane at different temperatures in order to obtain the activation energy of the process, and the value of the pre-exponent of the reaction rate constant.

EXPERIMENTAL

Experiments were carried out in a jet vacuum apparatus, the principal layout of which has been described in earlier papers [3]. Atomic oxygen was generated by high voltage discharge in molecular oxygen and was drawn through a nozzle into the reaction vessel. Molecular oxygen was prepared by heating $KMnO_4$ (chem. pure grade). The vessel holding the $KMnO_4$ was directly connected to the vacuum apparatus. The oxygen passed through a tube filled with glasswool and a trap, cooled with liquid nitrogen in order to remove moisture. Dichlorethane was introduced from a calibrated vessel into the reaction vessel through a tap-valve. Introduction could be effected at various distances from the nozzle, i.e., the point of entry of atomic oxygen into the reaction vessel. The reaction products were collected in a removable trap cooled by liquid nitrogen, and were subjected to analysis. Acid was determined by titration against alkali with phenolphthalein and in addition the amount of chloride-ion was determined by a separate titration according to Volhard's method. Carbon monoxide was analyzed in separate experiments as CO_2, frozen out in the trap, after passage of the jet-stream through a heated tube containing I_2O_5. Aldehydes were determined by titration with hydroxylamine hydrochloride. Formaldehyde was estimated in a photoelectric colorimeter after reacting it with chromotropic acid. The reaction temperature was measured by means of several thermocouples (copper-constantan) situated inside the reaction vessel at various distances from the nozzle.

Experiments were carried out in the absence of a flame reaction. If the reaction $O + CH_2Cl$ - CH_2Cl was carried out in a vessel which was untreated then the reaction took place with considerable evolution of heat up to 250-300°C. The considerable evolution of heat was usually accompanied by a flame reaction. With the aim of suppressing the flame reaction the walls of the vessel were subjected to pretreatment. They were coated with KCl and treated with the products of electrical discharge in water vapor and also with the products of the same reaction at the same time until appreciable evolution of heat was no longer observed.

Analysis of the products of the reaction of atomic oxygen with dichlorethane showed that the main reaction products were hydrogen chloride and CO. Analysis of a solution of the reaction products in water for acid and chloride-ion showed that no other acid besides HCl was formed in the reaction. In Table 1 are given representative results for the analysis of the reaction products.

TABLE 1

No. of exp.	Pressure mm Hg	$C_2H_4Cl_2 \cdot 10^{-18}$ mol./sec	Rate of accumulation, molecules/sec: HCl $\cdot 10^{-16}$	Aldehydes 10^{-16}	$CH_2O \cdot 10^{-16}$	CO $\cdot 10^{-16}$
253	4,6	4,2	115	11,5	3,4	—
255	4,3	4,58	118	8,5	3,1	—
290	4,2	4,75	120	8,5	2,1	—
234	6,5	1,65	52,5	—	—	38(90%)

Table 1, shows that aldehydes were produced by an order less than HCl. According to the aldehyde composition formaldehyde itself and apparently monochloracetaldehyde were present. The polarogram of the reaction products in buffered solution at pH = 10.17 - 11.4 revealed the presence of a wave at a potential corresponding to the reduction potential of monochloracetaldehyde. However, quantitative measurements, of the monochloracetaldehyde were not made. Experiments, like 234, were made with the aim of analyzing the carbon monoxide and comparison of the quantity of monoxide with the quantity of HCl. Since for the CO analysis the jet-stream was passed through a tube packed with I_2O_5, the pressure in the jet-stream was somewhat greater than in the usual experiments. Control experiments, made with pure carbon monoxide (without electrical discharge) with the aim of checking the completness of recovery of CO as CO_2 under out experimental conditions showed that there was a 90% recovery of the quantity of CO passed through. Thus the quantity of carbon monoxide produced in the reaction in comparison with the amount of HCl was 80%. Measurement of the rate constant of the reaction of atomic oxygen with dichlorethane was carried out by the method which we published earlier [3], by means of which the rate constants of the reaction of atomic oxygen with CO [4], CH_3OH [5], CH_3CHO [6] were measured.

According to this method the total rate constant of the reaction $O + C_2H_4Cl_2$ -k, which is itself the sum of the rate constants of the separate reaction courses, can be determined from the rate of accumulation of one of the primary reaction products. In the present case for the reaction $O + C_2H_4Cl_2$, the main primary reaction products are HCl and CO. On the basis of the method used to measure the rate constants, the absolute value k for the reaction $O + CH_2Cl = CH_2Cl$ is determined from the equation.

$$1/(HCl)_F = \frac{k}{k'(O)_0} + \frac{[k_0 + k_0'''(M)(O)_0]\,k}{k(C_2H_4Cl_2)_0 k'(O)_0}, \qquad (1)$$

where $(HCl)_F$ is the final HCl concentration; $(O)_0$ is the initial concentration of atomic oxygen; $(C_2H_4Cl_2)_0$ is the initial concentration of 1, 2-dichlorethane; $k_0 + k_0'''(M)(O)_0$ is the rate constant for linear destruction of atomic oxygen; k_0''' is the rate constant for quadratic destruction of atomic oxygen; M is the concentration of third particles i.e., molecular oxygen; k' is the rate constant of the reaction of atomic oxygen with dichlorethane, occurring with formation of HCl.

Equation (1) plotted with coordinates $1/(HCl)_F$ and $1/(C_2H_4Cl_2)_0$ is a straight line. The value $\frac{k}{k'(O)_0} = b$ is the intercept on the ordinate axis. The term $\frac{[k_0 + k_0'''(M)(O)_0]k}{k \cdot k'(O)_0}$ is the tangent of the angle of slope of the straight line which is the product of $\frac{[k_0 + k_0'''(M)(O)_0]}{k}$ with b i.e.,

$$\tan\alpha = \frac{[k_0 + k_0'''(M)(O)_0]}{k} \cdot b.$$

Hence the required value k is given by:

$$k = \frac{[k_0 + k_0'''(M)(O)_0] \cdot b}{\tan\alpha}. \qquad (2)$$

As seen from formula (2) in order to measure the value k, in addition to a plot of the graph with coordinates $1/(HCl)_F$; $1/C_2H_4Cl_2)_0$ it is necessary to know the total destruction of atomic oxygen. In this work the rate constant for the destruction of atomic oxygen was measured in the same way as in previous studies involving measurement of rate constants of reactions of atomic oxygen. In order to determine the total destruction of atomic oxygen it is necessary to measure the relative concentrations of atoms along the length of the reaction vessel x, i.e., it is necessary to know the dependence of $\frac{(O)_0}{(O)_x}$ on x. A detailed method of determining the sum $k_0 + k_0'''(M)(O)_0$ was

described in a paper on the study of the reaction O + CO [4]. The relative concentration of atomic oxygen was measured from the maximum yield of HCl on introducing dichlorethane at various points into the reaction vessel. One special feature may be noted in the measurement of the relative concentration of atomic oxygen in this work. The fact is, as experiments with dichlorethane showed, the dichlorethane and probably the reaction products of atomic oxygen with dichlorethane, specifically treat the surface, a layer of KCl, in such a way that destruction of atomic oxygen is decreased, and this results in much greater yields being observed of the primary product HCl, than yields of primary products in the case of the reaction of other substances in the same vessel.

In order that the measured destruction constant corresponded with that destruction for which measurements of the dependence of $1/(HCl)_F$ on $1/(C_2H_4Cl_2)_0$ were carried out, before each experiment for measurement of the concentration of atomic oxygen at a distance x from the nozzle, an additional experiment was carried out with introduction of dichlorethane in front of the nozzle.

Thus before each measurement of the concentration of atomic oxygen at a determined distance from the nozzle, the surface of the vessel was treated with dichlorethane and its reaction products with atomic oxygen at different points of the reaction vessel at a temperature of 160°C and pressure of 4.3 mm Hg. From Fig. 1, it is seen that the dependence of $\log\frac{(O)_0}{(O)_x}$ on x is a straight line. The straight line dependence of $\log\frac{(O)_0}{(O)_x}$ on $\underline{x}$ is evidence of the fact that the destruction of atomic oxygen is predominantly linear [4]. It may be noted that in any destruction of atomic oxygen that we measured, we only observed a linear destruction [4-6]. For the case of linear destruction, the destruction constant of atomic oxygen is determined from the tangent of the angle of slope of the straight line described in Fig. 1 by the formula:

$$k_0 = 2{,}3w \tan\gamma,$$

where w is the linear rate of the jet stream.

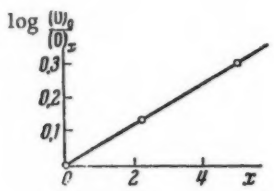

Fig. 1. Dependence of the relative concentration of atomic oxygen on distance from the nozzle.

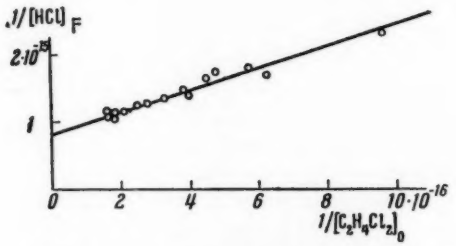

Fig. 2. Dependence of the reciprocal of the final concentration of hydrogen chloride on the reciprocal of the initial concentration of 1, 2-dichlorethane.

The destruction constant of atomic oxygen was measured at all the pressure and temperature conditions for which $\underline{k}$ was measured.

In Fig. 2 is shown the dependence of $1/(HCl)_F$ on $1/(C_2H_4Cl_2)_0$ at a temperature of 160°C and pressure 4.3 mm Hg. From the value of the intercept on the ordinate axis and the tangent of the angle of slope of the straight line in in Fig. 2, by applying formula $k = \frac{k_0 b}{\tan\alpha}$ the value of the rate constant was obtained for the reaction of atomic oxygen with 1, 2-dichlorethane at the indicated temperature of 433° K and pressure 4.3 mm. In the same way determinations were made of the constant $\underline{k}$ at other temperatures and pressures. The results of these measurements are given in Table 2.

Measurement of the rate constant for the reaction O + CH_2Cl - CH_2Cl carried out at a pressure of 2 mm, as Table 2 shows, did not result in a change in the reaction rate constant within the limits of experimental error.

In Fig. 3 the values of $\log\underline{k}$ are plotted against 1/T. The activation energy obtained from Fig. 3 equals 5500 ± 500 cals/M. Thus the following expression is obtained for the rate constant of the reaction O + CH_2Cl-CH_2Cl:

$$k = 2\cdot10^{-11} e^{-\frac{550}{RT}} \text{ cm}^3\cdot\text{sec}^{-1}\cdot\text{molecules}^{-1}.$$

In the present work side by side with measurements of the constant $\underline{k}$, determinations of the same constant were also made from the yield of formaldehyde. Since formaldehyde is formed in very small amount (100 times less than HCl) determinations of the constant are also somewhat less accurate than those for HCl. Nevertheless, we obtained a satisfactory agreement of the constants measured with respect to HCl with the constants measured with respect to CH_2O. Thus the constant $\underline{k}$ measured at 393° K for CH_2O equalled $0.9 \cdot 10^{-14}$ (for HCl $1.4 \cdot 10^{-14}$), at 473° K for CH_2O $\underline{k}$ equalled $6.5 \cdot 10^{-14}$ (for HCl $10 \cdot 10^{-14}$), Such agreement confirms the accuracy of the measured constant for the reaction $O + C_2H_4Cl_2$.

DISCUSSION

Unfortunately there are no other data relating to the rate constant of the reaction of atomic oxygen with dichlorethane. The value obtained for the rate constant can be compared with the rate constants for the reactions of atomic oxygen with methyl alcohol [5] and with acetaldehyde [6]. For the absolute value in the given temperature range the rate constant for dichlorethane differs little from the constants for CH_3OH and CH_3CHO. However the activation energy of the reaction of $O + C_2H_4Cl_2$ is somewhat above that of the reactions $O + CH_3OH$ (3100 cal) and $O + CH_3CHO$ (2750 cal).

We will consider the mechanism of the interaction of atomic oxygen with molecular dichlorethane. If account is taken of the fact that the main products of the reaction are HCl and CO, during which CO is produced in amount close to the amount of HCl then a mechanism may be assumed for the reaction $O + C_2H_4Cl_2$ analogous to the mechanism for the interaction of atomic oxygen with ethane [2]. In consequence of the fact that in the reaction $O + C_2H_6$ the main product is formaldehyde and also in consideration of other data for the interaction of $O + C_2H_6$ the following reaction was suggested:

$$O + CH_3{-}CH_3 \rightarrow CH_2O + H_2 + CH_2.$$

TABLE 2.

T.° K	p, mm Hg	k_0, sec^{-1}	$k \cdot 10^{14}$, $cm^3 \cdot sec^{-1}$ molecules
353	4,3	33	1,1
393	4,3	38,5	1,4
433	4,3	55	2 68
473	4,3	188	10
393	2	62	1,56

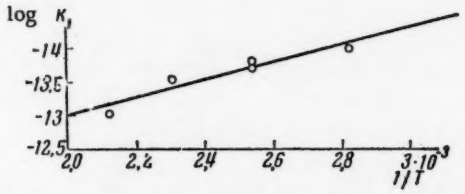

Fig. 3. Temperature dependence of the rate constant for the reaction of atomic oxygen with 1, 2-dichlorethane.

When molecular oxygen is present the radical CH_2 will interact with it. Earlier [2] it was assumed that the CH_2 radical reacted with an O_2 molecule in the following way:

$$CH_2 + O_2 \rightarrow CH_2O + O.$$

However by consideration of the accumulated experimental material concerning the reactions of atomic oxygen which we obtained after publication of the papers on the reactions of atomic oxygen with ethane [2] and ethylene [7] and on repetition of the experiments in the study of the reaction of these substances with atomic oxygen, we incline to the view that the radical CH_2 can react with molecular O_2 in space in the following way:

$$CH_2 + O_2 \rightarrow CO + H_2O$$

i.e.,with formation of carbon monoxide and water.

For the dichlorethane reaction, the interaction with atomic oxygen may be written down in the same way as for ethane, with the difference that instead of formaldehyde the compound $\begin{matrix} H \\ Cl \end{matrix}\!\!>\!CO$, will be produced, which being unstable will result in the observed reaction products HCl and CO.

$$O + Cl{-}\overset{H\ H}{\underset{H\ H}{C{-}C}}{-}Cl \rightarrow \begin{matrix} H \\ Cl \\ HCl + CO \end{matrix}\!\!>\!C{=}O + HCl + CH_2 \qquad (3)$$

the radical CH_2 with O_2 yields CO and H_2O

$$CH_2 + O_2 \rightarrow CO + H_2O. \qquad (4)$$

According to this scheme the main products will be HCl and CO arising in equivalent amounts. However reaction (3) can be written in the following way:

$$O + CH_2Cl{-}CH_2Cl \rightarrow \begin{matrix} H \\ Cl \\ HCl + CO \end{matrix}\!\!>\!C{=}O + H_2 + CHCl \qquad (5)$$

i.e., instead of HCl and CH_2, H_2 and CHCl are produced. The radical CHCl will react with O_2. Taking into consideration that no other acid besides HCl is experimentally obtained, the reaction of CHCl with O_2 must be written:

$$CHCl + O_2 \rightarrow CO_2^* + HCl. \qquad (6)$$

It is possible that the presence of the reaction path (5) together with (6) results in somewhat less CO being produced than HCl. The deficiency in the quantity of CO must equal the quantity of CO_2 formed.

The small amounts of monochloracetaldehyde could be explained by the reaction:

$$O + CH_2Cl{-}CH_2Cl \rightarrow \left[Cl{-}\overset{H\ H}{\underset{OH\ H}{C{-}C}}{-}Cl \right] \rightarrow HCl + \begin{matrix} O \\ \| \\ H \end{matrix}\!\!>\!C{-}CH_2Cl$$

This reaction represents the introduction of an oxygen atom across the C–H bond, which we have observed repeatedly for example in other compounds. The introduction product is itself an unstable compound which decomposes, since there are two functional groups Cl and OH attached to one carbon. Formation of CH_2O may be attributed to a reaction analogous to (3), but occurring with a very small probability:

$$O + CH_2Cl{-}CH_2Cl \rightarrow CH_2O + HCl + CHCl. \qquad (7)$$

Summing up it can be said that an oxygen atom reacts with molecular dichlorethane mainly with cleavage of the C–C bond, in the same way as occurs in the case of the reaction of atomic oxygen with ethane. The principal reactions are reactions (3) and subsequently reaction (4).

SUMMARY

1. Absolute values of the rate constant for the reaction of atomic oxygen with 1, 2-dichlorethane in the temperature range 353-473° K and at pressures of 2 and 4.3 mm Hg were measured. The activation energy of the reaction was determined.

2. In a study of the mechanism of the interaction of atomic oxygen with 1, 2-dichlorethane it was shown that the main reaction products were HCl and CO, formed in the primary act, resulting in cleavage of the C–C bond.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STRUCTURE AND SPECTRA OF VINYL SULFIDES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9,
pp. 1571-1577, September, 1961
Original article received December 29, 1961

Vinyl compounds of the type C=C-X−R are of great interest in the study of the reciprocal effects of atoms and groups because they have a comparatively simple structure; they may be discussed conventionally as a system of two interacting groups.

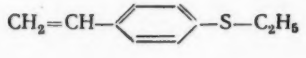
It would be very useful to carry out a systematic study of all possible compounds of this type using current physical methods. By this means it might be possible to observe the reciprocal effect of the group containing the π-bond and the group XR. The material so far available is not satisfactory for generalizations; only vinyl ethers [1] and vinylsilicon compounds [2] have been studied more or less thoroughly.

In this work the spectral data for compounds in which the double bond C = C is linked to a sulfur atom have been collected. Data for the absorption spectra in the infrared and near ultraviolet regions are available for some similar compounds [3-5]. As in the study of vinyl ethers, we used here the combination dispersion (raman spectra) and ultraviolet absorption spectra.

In Table 1 are compared; 1) the values of the frequency ($w_{C=C}$) for valence vibration of the double bond C = C in cm^{-1} (determined with the pure liquid substance); 2) the intensity coefficients of the C = C line in the raman spectrum ($I_{C=C}$); 3) the ultraviolet absorption spectra of solutions in heptane; λ-position of the absorption band maxima in angstrom units; ε-molar (decimal) absorption coefficient at the maximum; f the oscillator strength; in square brackets is given the position of the apex of the absorption curve (real position of the hidden maximum). The absorption curves are given in Figs. 1, 2, 3. For comparison data for two sulfides not containing double bonds (dicyclohexyl sulfide, diethyl sulfide) are included in Table 1.

From Table 1 it is clear that the double bond (C = C) frequency in the spectra of vinyl-n-alkyl sulfides is considerably lower than for alkenes-1 or vinyl ethers, and it lies in the 1586 cm^{-1} region. The differences in the C = C valence vibration frequency in the series of C = C-X-R compounds investigated could arise from differences in the rigidity of the C = C bond itself, from the incomplete localization of the vibration, and also from differences in the kinematic and dynamic parameters of the environment surrounding it (in particular, in the rigidity of the C-X bond, and in the mass of the atom X). Calculations on the simplest model of the molecule (taking into account only vibration of the chain and using conditions of constant rigidity of the C = C bond) it was shown that on changing CH_2=CH-$CH_2R \rightarrow CH_2$ = CH-SR one would expect a decrease in the double bond frequency of not more than 20-30 cm^{-1}, whereas the observed decrease is 50-55 cm^{-1}. This gives a basis for the conclusion that in vinyl-n-alkyl sulfides the sulfur atom affects the state of the double bond by somewhat decreasing its force constant.

Additional information may be obtained from the spectrum of p-mercaptoethylstyrene



where the SR group is not directly joined to the double bond and hence the effect of the mass of the sulfur atom on ($w_{C=C}$) should be extremely small, whereas the effect of SR on the rigidity and frequency of the C = C bond should be observed. According to the data of Table 2 a small decrease in ($w_{C=C}$) and an increase in intensity of the C=C line occur; this decrease in frequency is in agreement with the suggestion that the sulfur atom affects the rigidity

of the C=C bond in vinyl sulfides (or, in any case, does not conflict with this suggestion). In Table 2 data for some other p-substituted styrenes are included for comparison. These data also show that the C=C frequency is much less subject to the influence of p-substituents than the frequency of other groups, be they electropositive or electronegative (OH, NH_2, COR, NO_2). Comparison of the data on the C=C frequency shows that the introduction of branched aliphatic radicals has less effect on the C=C frequency of vinyl sulfides than on that of vinyl ethers. One of the reasons for the closeness of the C=C frequency in vinyl-t-butyl sulfide and vinylethyl sulfide is the comparatively large mass of the sulfur atom which, with the so called C=C vibration, should have a lower vibration amplitude than the oxygen atom in analogous compounds.

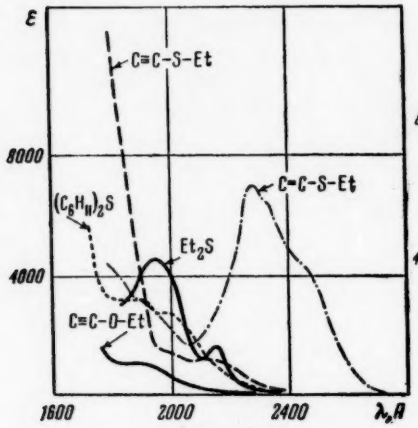


Fig. 1

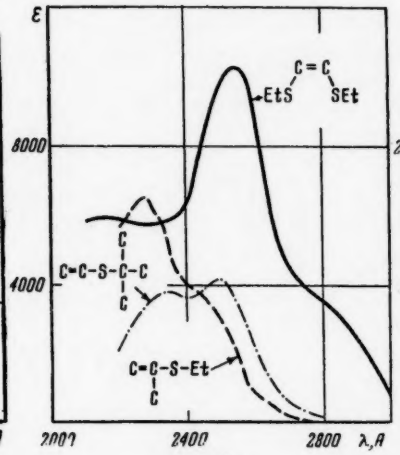


Fig. 2

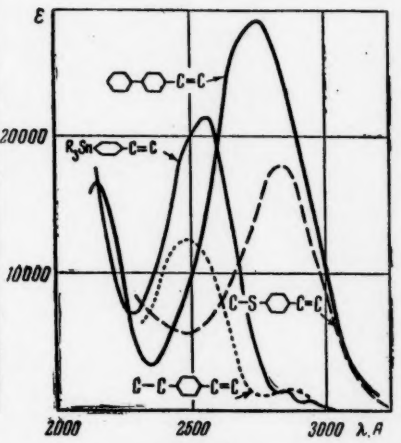
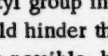


Fig. 3.

The introduction of an α-substituent and also the introduction of a branched alkyl group R into the radical SR should obviously have less effect on the geometric configuration of the vinyl sulfide molecule because the C–S interatomic distance is greater than the C–O distance and the steric factors here are less important.

An approximate calculation of the angle of rotation (θ) of the group C-S-R around the bond C-S relative to the plane $C=C\diagdown_{S}$ for n-alkylvinyl sulfides with the calculated interaction energy of the chemically not bonded but neighbouring atoms in the form of a Lennard-Jones potential and with the supposition that conjugation favors a planar form, showed that two forms are energetically most favorable: the planar S-trans (θ = 0°) and close to it the S-cis  with θ ~ 160°C. n-Alkyl groups in the α-position do not change the picture to any extent. A t-butyl group in the α-position should hinder the formation of a planar trans form, but in vinyl-t-butyl sulfide it should hinder the formation of the cis-form. In n-alkylvinylethers the existence of a planar trans-configuration is also possible; however in this case steric hindrance in the planar cis- form should affect the O-R bond more strongly and the real angle of rotation of O-R should differ more from 180°C than the angle of rotation of S-R.

The simultaneous presence of two rotational isomers should cause the appearance of doublets in the vibration spectra. Because the mass of the S atom is greater than the mass of the O atom it would be expected that the $w_{C=C}$ should be less separated in vinylsulfides; on the other hand the stronger interaction between C=C and SR might lead to the reverse. Using the ordinary three prism spectrograph the splitting of the C=C raman line in vinyl sulfides was not observed. However with an instrument of greater dispersing power signs of splitting were observed at a relatively low temperature (~ -40°).

The introduction of a methyl group into the α-position in the molecule of 1-alkenes, vinylsilanes, vinyl ethers, and vinyl sulfides led to an increase in $w_{C=C}$ by 10-40 cm^{-1} (Table 1). The largest spectral change was observed with vinyl ethers. α-Substituents can evidently affect the position of the equilibrium between the rotational isomers. However comparison of the data in Table 1 and the absence of noticeable splitting of the C=C line in vinyl sulfides provides a basis for thinking that in vinyl sulfides at least, this is not the chief reason for spectral changes; also it is unlikely that an α-alkyl group would have an important effect on the rigidity of the C=C bond. Evidently the change in frequency is here connected with some change in the form of vibration. In this connection one must pay attention to the fact that α-substituents affect the absorption spectra of all the types of vinyl compound described here in the

same way, decreasing somewhat the absorption intensity at the band maxima and moving the bands towards the visible region of the spectrum. The effect of a t-butyl group has the same character in the molecules

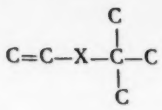


TABLE 1.

Molecular structure	Raman spectra**		UV Absorption spectra***		
	$\omega_{C=C}$	$I_{C=C}$	λ_{max}	ε	f
C=C–C–C–C–C	1642	40	1800	11000	0.24
C=C–C–C–C–C (C branch)	1654	40	1885	9000	0,21
C=C–O–C–C–C–C	1610 1636 1653	50	1920	9600	0,27
C=C–O–C(C)(C)–C	1636	100	2000	8000	0,22
C=C–O–C(C)–C	1600 1659	50	1970	8800	0,34
C–C–S–C–C	—	—	1940 2150	4800 1600	0,19 —
C_6H_{11}–S–C_6H_{11}*	—	—	1910	3200	
C=C–S–C–C	1586	60	2280 [2400]	7000 4000	0,19
C=C–S–C–C–C	1586	—	2280 [2400]	5400 4300	0,17
C=C–S–C–C–C–C	1586	60	2280 2400	6600 5000	0,17
C=C–S–C(C)(C)–C	1586	—	2340 2490	3900 4300	0,10 0,12
C=C–S–C–C (C branch)	1612	62	2280 [2450]	6500 4000	0,16
C–C–S–C=C–S–C–C (cis)	1546	300	2540 [2850]	10300 3000	0,24

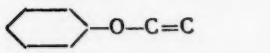
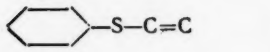
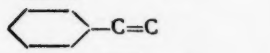
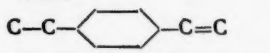
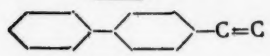
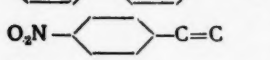
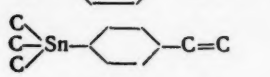
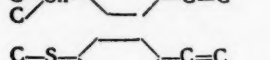
* Dicyclohexylsulfide.

** The raman spectra were obtained on an ISP-51 spectrograph and a large three prism spectrograph ISP-67 which has a linear dispersion of 22 A/mm in the 4860 A region. The exciting frequency was mercury 4358 A. Solutions in CCl_4 containing 1 M of substance in 1 M solvent were used to determine the intensity. As unit intensity was taken 1/100th of the intensity of CCl_4 313 cm^{-1} line calculated at 1 M. A photoelectric spectrophotometer, with an accuracy of ~ ± 15%, was used.

*** The absorption spectra were measured with CF-4 and SP-41 spectrophotometers. The latter incorporates a vacuum double monochromator and an LiF prism. The solvent was heptane.

The data on the absorption spectra of hexene and isoheptene are taken from the paper [6] and on the spectra of diethyl sulfide from [5].

TABLE 2.

Molecular structure	Raman spectra w, cm^{-1} C≡C	b. F.*	Raman spectra I C≡C	b. F.*	UV absorption spectra (in heptane) λ, A**
	1643	1592	58	42	2790 (1,2)
	—	—	—	—	2660 (8,5), 2500 (8,3)
	1631	1600	300	240	2820 (0,8), 2460 (13), 2030 (24)
	1632	1605	320	170	2850 (0,8), 2490 (12,5)
	1629		~800		2760 (28,5), 2150 (16)
	1632	1598	—	—	2890 (15,6)
	1629	1590	900	800	2560 (21,2)
	1630	1598	650	—	2840 (18)

* Benzene ring line.

** The value $\frac{\varepsilon \max}{1000}$ is given in brackets. Several maxima occur in the 2800-1900 A region in vinylphenylether, stryene and ethylstyrene, in Table 2 the most intense components are given. E. A. Chernyshev kindly presented the tin compound.

TABLE 3.

Substance	Raman spectrum Frequency cm^{-1}	Intensity	UV-spectra λ	ε
HC≡C—R **	2118	110	1800	4 000
HC≡C—O—C_2H_5	2152	~ 60	1880	1 180
HC≡C—S—C_2H_5	2178	200	1800***	11 000***
HC≡C—C_6H_5	2050	—	1990	33 000
	2106		2350	15 000
			2460	14 000

* See Figs. 1 and 4.

** Mean value from literature data.

*** Not a maximum.

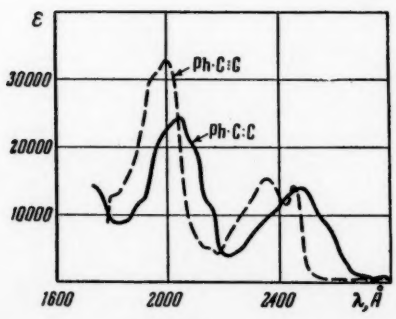
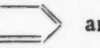
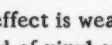
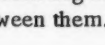


Fig. 4.

A comparison of the absorption spectra cited in Table 1 shows that the absorption bands lie closer to the visible region of the spectrum in alkyl-vinyl sulfides than in vinylethers, alkenes and dialkylsulfides (see Figs. 1, 2). Thus additivity of absorption is not observed here (this is evidently a result of the reciprocal effects of the C=C and SR groups, which can be described as conjugation of the π-electrons of the double bond and an unshared pair of electrons of the S atom). In agreement with this the intensity coefficients of the C=C raman lines ($I_{C=C}$) of vinylalkylsulfides are sufficiently high. Note that a large value of $I_{C=C}$ may not be attributed to participation of the C-S bond in the incompletely localized "C=C vibration" because the signs of the amplitudes

of the unitary coordinates $q_{C=C}$ and q_{C-S} are opposite to one another.

The ratios of the intensity coefficients ($I_{C=C}$) (see Table 1) of the different vinyl compounds agree qualitatively with expectations, judging from absorption spectra. However they are quantitatively satisfactory only in series of a single type of compound e.g. in a series of vinyl sulfides or a series of vinyl ethers.

Taking into account all the above remarks one can say that the SR group has a stronger effect than the OR group on the optical properties of vinyl compounds and it has a stronger effect on the C=C double bond both in the ground and electronically excited states. In a similar way the group SR has a more important effect than OR on optical properties of molecules of the type RX–  and RX–  –NO_2 the SR group is ortho-para-directing in the aromatic nucleus but its directing effect is weaker than that of the corresponding oxygen compound. A systematic study of additions to the double bond of vinyl sulfides also led to the conclusion that the electron donor properties of the SR group are weaker than those of the OR group. Data from a study of dipole moments (from which properly speaking, one should judge the electron donating abilities of a group) show that both groups are clearly electropositive and there is no great difference between them. Also there is no great difference between the effect of SR and OR on the frequency of the nitrogroup in molecules of the type RX–  –NO_2 [8]. The difference in the observed reciprocal effects of the atomic groups in their physical and chemical properties is not surprising; the different properties may be determined by the parameters of different states of the molecule (thus, the optical properties are determined by the parameters of the electronically excited levels). It should be noted that in some ionic reactions of vinyl sulfide the sulfur atom can play the part of a secondary reaction center, linked to the catalyst [9]; thus the observed reactivity does not permit one to judge directly the effect of the S atom on the state of the double bond.

In Table 2 data on vinyl sulfide are cited. The molecule of this compound is evidently nonplanar, even though the degree of hindrance to coplanarity ought to be considerably less than in vinylphenylether in which the angle of rotation of the benzene ring relative to the C=C plane should exceed 30°C. Thus there is no superposition of the lines given from $I_{C=C}$ of vinylphenylsulfide. By comparison of the absorption spectra, it is noticed that it differs somewhat from that of methylphenylsulfide. However, the absorption spectrum of vinylphenylsulfide is similar to that of anisole.

In Table 3 are cited the spectra of some acetylene derivatives. It is interesting that the OR and SR groups not only do not lower the frequency of the double bond - on the contrary they actually raise it. This gives a reason for thinking that the rigidity of the triple bond is here somewhat increased. However the effect of the OR group on the absorption spectra of compounds with double and triple bonds is similar; one can say the same about the effect of the SR group.

SUMMARY

1. An SR group directly connected to a C=C double bond decreases the C=C frequency and evidently lowers the rigidity of this bond; at the same time it increases the frequency of the C=C triple bond. The SR group has a stronger effect than the OR group on the C=C and C≡C frequencies and on the optical parameters of the molecule.

2. Steric hindrance should have a smaller value in alkylvinylsulfide molecules than in vinyl ethers. The alkylvinylsulfide molecules are most likely to exist as the planar S-trans form or the nearly S-cis form.

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ISOPROPENYL AND VINYL DERIVATIVES OF TRI- AND PENTA-VALENT ANTIMONY

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1578-1582, September, 1961
Original article received February 15, 1961

In our preceding paper [1] we described the synthesis of a series of cis- and trans-propenyl derivatives of tri- and penta-valent antimony and we have reported [2] the preparation of pentavinylantimony. In the present work we are able to describe the synthesis of a series of isopropenyl (1-methylvinyl) and vinyl antimony derivatives of the types

$$R_3Sb,\ R_5Sb,\ R_4SbX,\ R_3SbX_2, \text{ where } R \rightarrow CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}- \qquad (1)$$

$$CH_2=CH-;\ X=Cl,\ Br,\ I$$

By the reaction of isopropenyl lithium and vinylmagnesium bromide [3] with antimony trichloride triisopropenylantimony and trivinylantimony respectively were obtained

$$3CH_2=C\begin{matrix}Li\\ \diagup\\ \diagdown\\ CH_3\end{matrix} + SbCl_3 \rightarrow \left(CH_2=C\begin{matrix}\diagup\\ \diagdown\\ CH_3\end{matrix}\right)_3 Sb + 3LiCl \qquad (2)$$

$$3CH_2=CHMgBr + SbCl_3 \rightarrow (CH_2=CH)_3Sb + 3MgClBr$$

and these reacted easily with halogens to give reaction products containing pentavalent antimony

$$R_3Sb + X_2 \rightarrow R_3SbX_2 \qquad (3)$$

The reactions of triisopropenylantimony dibromide with isopropenyl lithium and of trivinylantimony dibromide with vinylmagnesium bromide led respectively to pentaisopropenylantimony and pentavinylantimony:

$$\left(CH_2=C\begin{matrix}\diagup\\ \diagdown\\ CH_3\end{matrix}\right)_3 SbBr_2 + 2CH_2=C\begin{matrix}Li\\ \diagup\\ \diagdown\\ CH_3\end{matrix} \rightarrow \left(CH_2=C\begin{matrix}\diagup\\ \diagdown\\ CH_3\end{matrix}\right)_5 Sb + 2LiBr$$

$$(CH_2=CH)_3SbBr_2 + 2CH_2=CHMgBr \rightarrow (CH_2=CH)_5Sb + 2MgBr_2 \qquad (4)$$

These compounds were isolated after evaporation of the ether, extraction of the reaction mass with petrol ether, and distillation of the latter. The liquid pentaalkenylantimonys were thus obtained in a sufficiently pure state as indicated by elementary analysis.

By treatment of pentaisopropenyl-and pentavinyl-antimony with an equimolecular quantity of bromine tetraisopropenylstibonium and tetravinylstibonium bromide respectively were obtained, and on treatment with an equimolecular quantity of iodine, tetraisopropenylstibonium and tetravinylstibonium iodide were obtained.

$$R_5Sb + X_2 \rightarrow R_4SbX \qquad (5)$$
$$X = Br, I$$

When pentaisopropenyl- or pentavinyl-antimony were heated at 180°C for 40 min triisopropenylantimony and trivinylantimony respectively were obtained. This was demonstrated by initial bromination of the residue, followed by distillation. In this way triisopropenylantimony dibromide (m.p. 137-138°C) and trivinylantimony dibromide (n_D^{30} 1.6460) were separated.

Trivinyl- and triisopropenyl-antimony reacted with thallium trichloride to give respectively trivinyl- and triisopropenylantimony dichloride, and thallium was separated as the monochloride:

$$R_3Sb + TlCl_3 \rightarrow R_3SbCl_2 + TiCl: \quad (6)$$

$$R \rightarrow CH_2 = CH-;\ CH_2 = C\begin{matrix}\diagup \\ \diagdown\ CH_3\end{matrix}$$

EXPERIMENTAL

Triisopropenylantimony.* To isopropenyl lithium, obtained from 20.0 g (0.1653 M) isopropenyl bromide and 2.2 g (0.3170 M) lithium in 150 ml dry ether at 5-10°C, was added dropwise a solution of 10.0 g (0.0439 M) antimony trichloride in 50 ml ether at 15-20°C during 40 min. After 4 hours stirring at room temperature the reaction mass was decomposed with 150 ml saturated ammonium chloride at 0-15°C. The ether layer was washed with water, and dried with calcined calcium chloride. After evaporation of the solvent the residue was distilled in vacuum. The fractions collected were I-to 40°C (1 mm), 1.33 g; n_D^{20} 1.5440; II - 40°C (1 mm); 7.0 g (66%); n_D^{20} 1.5475; d_4^{20} 1.2879; the residue 0.95 g. Found: C 44.08; 44.22; H 6.19; 6.24% C_9H_5Sb. Calculated: C 44.12; H 6.17%. The substance dissolved in ether, petroleum ether, chloroform, and benzene. It did not ignite in air but rapidly became turbid.

Trivinylantimony.* A solution of 25.0 g (0.1096 M) antimony trichloride in 25 ml tetrahydrofuran was added over 70 min to a Grignard reagent prepared from 10.0 g (0.4112 M) Mg in 50 ml tetrahydrofuran and 50.0 g (0.4674 M) vinyl bromide in 50 ml tetrahydrofuran. The temperature was maintained at 40-53°C. After 4 hours heating at 60°C the reaction mixture was cooled to 30°C and 50 ml ether and 150 ml 3% HCl added. The ether layer was separated and the aqueous solution extracted twice with 50 ml ether. The ether extracts were combined, washed twice with water, and dried with calcium chloride. The ether was evaporated and the residue distilled in vacuum. The fractions obtained were; I – to 46°C (15 mm); 0.70 g; n_D^{20} 1.5370; II – 46°C (15 mm); 11.3 g (51%); n_D^{20} 1.5614; d_4^{20} 1.4341; residue 3.0 g. Found: C 35.79; 35.77; H 4.57; 4.44%. C_6H_9Sb. Calculated: C 35.52, H 4.47%.

The reaction between triisopropenylantimony and thallium trichloride. A solution of 1.268 g (0.0041 M) thallium trichloride in 5.0 ml ether was added to 1.0 g (0.0041 M) triisopropenylantimony in 5.0 ml ether at room temperature. Thallium monochloride (0.96 g, 98%) and 0.98 g (76%) of a white crystalline substance with m.p. 102-103°C were separated. Found: C 34.25; 34.08; H 4.70; 4.65; Cl 23.39; 23.50%. $C_9H_{15}SbCl_2$. The substance dissolved well in chloroform, ethanol, and acetone, poorly in ether; it was insoluble in petroleum ether.

The reaction between trivinylantimony and thallium trichloride. A solution of 3.06 g (0.0098 M) thallium trichloride in 10 ml ether was added at room temperature to 2.0 g (0.0098 M) trivinylantimony in 10 ml dry ether. 2.23 g (99%) of thallium monochloride and 2.2 g of a liquid substance were separated. On distillation in vacuum the following fractions were obtained: I - to 102.5°C (3 mm); n_D^{20} 1.5870; weight 0.4 g; II - 102.5 -103°C (3 mm); n_D^{20} 1.5875; d_4^{20} 1.67278; weight 1.78 g (68%); residue 0.2 g. Found: C 26.25; 26.38; H 3.16; 3.27% $C_6H_9SbCl_2$. Calculated: C 26.32; H 3.31%.

Triisopropenylantimony dichloride. Dry chlorine was passed into a solution of 2.0 g (0.0082 M) triisopropenylantimony in 15 ml chloroform at a rate of 90 bubbles per minute at 0°C until the solution was colored pale yellow and the smell of triisopropenylantimony had disappeared. After evaporation of the chloroform the residue was recrystallized from 20 ml ether. Long needle-like crystals (1.97 g, 72%) with m.p. 102.5-104°C were obtained. A mixed melt with triisopropenylantimony dichloride from a previous experiment gave no depression of the melting point.

Triisopropenylantimony dibromide. A solution of 0.65 g (0.0041 M) bromine in 5.0 ml chloroform was added dropwise at 0°C to a solution of 1.0 g (0.0041 M) triisopropenylantimony in 5 ml chloroform. The chloroform was evaporated and the residue recrystallized from 5 ml carbon tetrachloride. A white crystalline substance (1.21 g, 73%) with m. p. 138°C separated out . Found: C 26.95; 26.92; H 3.72; 3.68; Br 40.98; 41.09%. $C_9H_{15}SbBr_2$. Calculated: C 26.70; H 3.73; Br 34.48%. The substance dissolved well in chloroform and acetone, less well in methanol and ethanol, poorly in ether, and not at all in petroleum ether.

* All operations in the experiments marked with an asterisk were carried out in a stream of pure, dry nitrogen.

Triisopropenylantimony diiodide. A solution of 1.04 g (0.0041 M) iodine in 15 ml ether was added at 0 to -5°C to a solution of 1.0 g (0.0041 M) triisopropenylantimony in 5 ml ether, 1.3 g (63%) of a crystalline substance which appeared slightly colored in yellow light was separated; m.p. 162-164°C. Found: C 22.02; 21.88; H 2.97; 2.99%. $C_9H_{15}SbI_2$. Calculated: C 21.67; H 3.03%. The substance dissolved well in chloroform, poorly in ether, and was insoluble in petroleum ether.

Trivinylantimony dibromide. A solution of 7.9 g (0.0494 M) bromine in 50 ml chloroform was added with stirring to 10.0 g (0.0492 M) trivinylantimony in 50 ml chloroform over 1.5 hr at 0 to -5°C. After evaporation of the chloroform the residue was distilled in vacuum. The fractions collected were I-115-117°C (1.5 mm); 2.75 g; n_D^{20} 1.6455; II-117-119° (1.5 mm); 13.4 g (74%); n_D^{20} 1.6480; d_4^{20} 2.11529; residue 1.05 g. Found: C 20.00; 19.86; H 2.56; 2.48%. $C_6H_9SbBr_2$. Calculated: C 19.87; H 2.50%.

Trivinylantimony diiodide. A solution of 0.63 g (0.00248 M) iodine in 10 ml ether was added at 0°C to 0.5 g (0.00246 M) trivinylantimony in 5 ml ether. Part of the ether was evaporated, and the residue was cooled to 0°C to give 0.86 g (63%) of small crystals which were colored in yellow light; m.p. 35-37°C. The substance dissolved well in chloroform, poorly in ether, and was insoluble in petroleum ether.

Pentaisopropenylantimony.* Isopropenyl lithium (prepared from 0.7 g (0.1009 M) lithium in 50 ml ether and 6.0 g (0.0496 M) propenylbromide in 6 ml dry ether) at 5-10°C was added dropwise over 45 min to a solution of 8.0 g (0.0197 M) triisopropenylantimony dibromide in 50 ml dry ether at -10 to -15°C. The mixture was stirred for 3.5 hr at -5 to 0°C. The ether was evaporated from the reaction mixture at the water pump without heating. The residue in the flask was extracted many times with petroleum ether (b.p. 35-45°C). The residue was filtered on a Shott funnel and washed with petroleum ether. Petroleum ether was evaporated from the filtrate at the water pump without heating. The residue, cooled with solid carbon dioxide, was filtered to give 4.5 g (69*) of a white amorphous substance, m.p. 60°C. Found: C 54.92; 54.62; H 7.66; 7.68% $C_{15}H_{25}Sb$. Calculated: C 55.07; H 7.7%. The substance dissolved very well in petroleum ether, chloroform, and ether, and poorly in methanol and ethanol. Water decomposed it to give a strongly alkaline solution.

Pentavinylantimony*. Vinylmagnesium bromide, which was prepared from 1.34 g (0.0550 M) Mg in 10 ml tetrahydrofuran and 6.0 g (0.0560 M) vinyl bromide in 6 ml, diluted with 25 ml tetrahydrofuran and cooled to room temperature, was added dropwise over 30 min to a solution of 7.0 g (0.0199 M) trivinylantimony dibromide in 7 ml tetrahydrofuran at -5 to -2°C. The reaction mixture was stirred for 3.5 hours at -5 to 0°C, cooled with solid carbon dioxide, and filtered. The residue was washed with ether and petroleum ether. The solvents were evaporated to a liquid residue which appeared slightly colored in green light. Weight 3.93 g (79%); n_D^{20} 1.5590; d_4^{20} 1.2986. Found: C 46.34; 46.27; H 5.86; 5.83%. $C_{10}H_{15}Sb$. Calculated: C 46.74; H 5.88%. Pentavinylantimony dissolves well in petroleum ether, chloroform, and ether, less well in methanol, and ethanol. Water decomposes it to give a strongly alkaline solution.

Tetraisopropenyl stibonium bromide. A solution of 0.84 g (0.0053 M) bromine in 10 ml chloroform was added dropwise to a solution of 1.75 g (0.0053 M) pentaisopropenylantimony in 10 ml chloroform cooled to -5°C. Part of the solvent was evaporated and 10 ml cold ether added to the residue. The glistening plate-like crystals were filtered off and washed with ether. Weight 1.44 g (73%), m.p. 125-135°C. Found: C 39.50; 39.53; H 5.57; 5.52%. $C_{12}H_{20}SbBr$. Calculated: C 39.38; H 5.51%.

Tetravinylstibonium bromide. A solution of 0.3 g (0.0019 M) bromine in 5 ml chloroform was added at -5°C to 0.5 g (0.0012 M) pentavinylantimony in 5 ml chloroform. Most of the chloroform was evaporated and 3 ml cold ether added. Thin needle shaped crystals separated - 0.39 g, 64% m.p. 53-54°C. Found: C 30.83; 31.00; H 3.87; 3.95%. $C_8H_{12}SbBr$. Calculated: C 31.01; H 3.90%.

Tetraisopropenylstibonium iodide. A solution of 0.39 g (0.0015 M) iodine in 5 ml ether was added to 0.5 g (0.0015 M) pentaisopropenylantimony in 5 ml chloroform at room temperature. The solvents were evaporated off and the residue was dissolved in 2.5 ml chloroform and reprecipitated with 2.5 ml cold ether. 0.51 g (80%) of a crystalline substance with m.p. 163-164°C was separated. Found: C 34.90; 34.89; H 4.83; 4.75%. $C_{12}H_{20}SbI$. Calculated: C 34.89; H 4.88%.

Tetravinylstibonium iodide. A solution of 0.49 g (0.0019 M) iodine in 5 ml ether was added at room temperature to 0.5 g (0.0019 M) pentavinylantimony in 5 ml chloroform. After removal of the solvents the residue was dissolved in 2.5 ml chloroform and reprecipitated with 2.5 ml cold ether. White crystals (0.56 g, 80%) with m. p.

* All operations in the experiments marked with an asterisk were carried out in a stream of pure, dry nitrogen.

68-70°C were obtained. Found: C 27.04; 27.03; H 3.42; 3.36%. $C_8H_{12}SbI$. Calculated: C 26.92; H 3.39%.

Tetraisopropenyl- and tetravinyl-stibonium bromides and iodides dissolve well in water acetone, methanol and ethanol, with difficulty in ether, and not at all in petroleum ether.

The effect of heat on pentaisopropenylantimony. 1.0 g (0.0031 M) of pentaisopropenylantimony was heated on an oil bath at 180°C for 40 min. The residue in the flask (0.66 g, 88%, n_D^{20} 1.5470) was reacted with one mole of bromine. In this way 0.99 g (91%) of a substance with m. p. 137-138°C was obtained. A mixed melt with triisopropenylantimony dibromide gave no depression of the melting point.

The effect of heat on pentavinylantimony. 1.0 g (0.0039 M) of pentavinylantimony was heated in conditions similar to those used for pentaisopropenylantimony. At 104-110°C a colorless strongly smelling liquid with n_D^{20} 1.5595 passed into the trap; weight 0.68 g (90%). After bromination 0.97 g (95%) of a liquid which was slightly colored in yellow light was obtained; n_D^{20} 1.6460. Trivinylantimony dibromide has n_D^{20} 1.6480.

SUMMARY

1. The synthesis of triisopropenylantimony from isopropenyl lithium and antimony trichloride, and its conversion by halogens into $(CH_2=C-CH_3)_3SbX_2$ are described.

2. Pentaisopropenylantimony has been obtained by the reaction of triisopropenylantimony dibromide with isopropenyl lithium; with bromine it gives tetraisopropenylstibonium bromide.

3. Pentavinylantimony has been synthesized by the reaction of trivinylantimony dibromide with vinylmagnesium bromide. An equivalent quantity of bromine converts it into tetravinylstibonium bromide.

4. The reaction between trivinyl- and triisopropenylantimony and thallium trichloride led to trivinyl- and triisopropenyl-antimony dichloride respectively. Thallium separated as its monochloride.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE REACTION OF FREE RADICALS WITH ASYMMETRIC ORGANOMERCURY COMPOUNDS

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Translated from Izvestiya Akademii Nauk, SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1582-1589, September, 1961
Original article received March 11, 1961

A number of authors have studied the relative rates of abstraction of the radical R as RH by hydrogen ions from organomercury compounds, R_2Hg [1-5]. By studies on this type of reaction using asymmetric organomercury compounds, RHgR', Kharasch [6, 7] was able to establish his electronegativity series for radicals in which the radical R is more electronegative than R' if it undergoes attack by the hydrogen ion to form RH.

Since organomercury compounds are known to react with free radicals it appeared interesting to study an example of a reaction of a free radical with a series of asymmetric organomercury compounds. This would give an order of removal by radical reagents (not by ions, as in the papers cited) and the corresponding radical series could be constructed.

We chose the reaction between carbon tetrachloride and organomercury compounds, initiated by benzoyl peroxide, which was discovered by one of us [8]. The stoichiometry of the reaction is described by the equation

$$R_2Hg + CCl_4 \rightarrow RHgCl + RCCl_3 \qquad (1)$$

We applied this reaction to a series of compounds of the type RHgR' which are cited in the table. These compounds were synthesized either by the method of one of us, Friedlina and Kocheshkov [9] (11, 12, 13, 14), or by the Grignard reaction (the rest). The following asymmetric organomercury compounds have been prepared for the first time; benzylhexylmercury, ethyl-n-butylmercury, α-naphthylmethylmercury, n-butylbenzylmercury, phenylbenzylmercury, and n-butylcyclohexylmercury.

In the reaction $RHgR' + CCl_4 \rightarrow RHgCl + R'CCl_3$ the free radical CCl_3 is bonded in each case in higher yield with the radicals standing on the left than with their right hand neighbors in the following series of radicals:

$$2,4,6\text{-}(CH_3)_3C_6H_2,\ \alpha\text{-}C_{10}H_7,\ p\text{-}CH_3C_6H_4,\ o\text{-}CH_3C_6H_4,\ m\text{-}CH_3C_6H_4,$$
$$C_6H_5,\ C_2H_5,\ C_4H_9,\ C_6H_5CH_2,\ C_6H_{11}.$$

In cases where radicals are far apart from one another in the series the process goes in one direction only and in almost quantitative yield. It is not difficult to see the close similarity of this series with Kharasch's series. The interpretation of this series in terms of a radical chain reaction is not as simple as in the heterolytic Kharasch reaction. It is difficult to give any interpretation of the course of the chain reaction other than that expressed by the equations

$$\begin{aligned}
(C_6H_5COO)_2 &\rightarrow C_6H_5^{\cdot} + C_6H_5COO + CO_2\\
C_6H_5^{\cdot} + CCl_4 &\rightarrow C_6H_5Cl + CCl_3^{\cdot}\\
CCl_3^{\cdot} + RHgR' &\rightarrow RHg^{\cdot} + R'CCl_3\\
RHg^{\cdot} + CCl_4 &\rightarrow RHgCl + CCl_3^{\cdot}\ \text{etc.}
\end{aligned} \qquad (2)$$

Consequently the step which determines the course of the reaction is

$$RHgR' + CCl_3 \rightarrow R'CCl_3 + RHg'$$

since the only further part played by the free radical RHg is to regenerate the trichloromethyl radical.

Thus the radical series based on decreasing affinity for the proton coincides with the radical series based on decreasing affinity for the free radical CCl_3.

EXPERIMENTAL

The reactions between asymmetric organomercury compounds and carbon tetrachloride in the presence of benzyl peroxide as initiator were carried out as follows. A weighed quantity (5-10 g) of the organomercury compound, $RHgR^1$, and 0.4-0.8 g benzoyl peroxide in 80-120 ml dry carbon tetrachloride were heated in an ampoule (which had been sealed when cooled), being mixed in a preheated water bath at 90°C and then heated on a boiling water bath for 8 hours. The ampoule was cooled and then opened. A crystalline deposit plus traces of metallic mercury were formed. The pure organomercury chloride was obtained immediately, free from traces of metallic mercury, by recrystallization from alcohol or acetone in most cases. Carbon tetrachloride was evaporated from the filtrate, and the residue was treated with 20% aqueous alkali on a boiling water bath for 2 hours. The residual carbon tetrachloride was separated from the aqueous alkaline solution which was then acidified with hydrochloric acid. In this way the crystalline carboxylic acid, formed from $RCCl_3$, precipitated out and was separated in the normal manner. The residual carbon tetrachloride was distilled off at the water pump under reduced pressure. Crystals of hexachloroethane remained on the walls of the flask. After sublimation they had a melting point and mixed melting point of 185°C (sealed capillary). The solvent, which was collected in a trap cooled to -20°C, was nitrated. 2, 4-Dinitrochlorobenzene with melting point and mixed melting point of 51°C was obtained.

The reaction of a mixture of two symmetric organomercury compounds with carbon tetrachloride in the presence of benzoyl peroxide was carried out as described below for dinaphthylmercury and di-m-tolylmercury. A mixture of 2.38 g (0.00522 M) di-α-naphthylmercury, 2.0 g (0.00522 M) di-m-tolylmercury, and 0.4 g benzoyl peroxide in 250 ml absolute carbon tetrachloride was heated at 76°C for 3.5 hours in a flask fitted with a reflux condenser closed with a calcium chloride tube. The reaction mixture was cooled to room temperature and the carbon tetrachloride evaporated at the water pump. The residue was treated with 20 ml petroleum ether (b.p. 40-60°C). In this way α-trichloromethylnaphthalene, m-trichloromethyltoluene, and hexachloroethane went into solution. The residue was filtered, and the solvent evaporated from the filtrate. The oily residue was treated with 20 ml 20% alcoholic alkali on a heated water bath for one hour. The alcohol was evaporated and the salts of α-napthoic and m-toluic acids formed were washed with ether and dissolved in a small amount of water. The solution was acidified with hydrochloric acid to give a precipitate of a mixture of α-napthoic and m-toluic acids. By fractional crystallization from 50% aqueous ethanol substances were separated with m.p. 159-160°C (0.2 g mixed melt with authentic α-naphthoic acid gave no depression; literature data [10]; m.p. 160-161°C) and m.p. 108-109°C (0.1 g mixed melt with authentic m-toluic acid gave no depression; literature data [11]: m.p. 110°C).

The rest of the reaction mixture, which contained the organomercury compounds and the unconsumed benzoyl peroxide, was treated by heating for 15 min with 1.2 g hydroquinone and 50 ml ethanol to decompose the benzoyl peroxide [12]. 100 ml water was added to precipitate α-naphthylmercury chloride, m-tolylmercury chloride and the unconsumed organomercury starting materials. To separate these products the precipitate was treated by heating on a boiling water bath with 120 ml glacial acetic acid for one hour [13] *. Water (180 ml) was added to the solution, and after cooling and standing for 10 hours a precipitate came down. Fractional crystallization (from benzene) of the precipitate yielded 0.81 g (49.5%) m-tolylmercury chloride with m.p. 158-159°C (literature data [1]: m.p. 159-160°C) and 1.55 g (82%) α-naphthylmercury chloride with m.p. 188-189°C. A mixed melt with authentic α-naphthylmercury chloride gave no depression of the melting point (literature data [14]; m.p. 188-189°C). The acetic acid solution was treated with aqueous sodium chloride, and the precipitate was recrystallized from ethanol to give 0.5 g (30.5%, based on initial di-m-tolylmercury) of a substance with m.p. 158-159°C. A mixed melt with authentic m-tolylmercury chloride gave no depression.

Benzylcyclohexylmercury. Cyclohexylmercury bromide (9.0 g 0.025 M) was added in small portions at 0-5°C to a vigorously stirred solution of the Grignard reagent prepared from 6.3 g (0.05 M) benzyl chloride and 1.2 g (0.05 M) magnesium in 100 ml dry ether. After stirring for two hours and standing overnight at 0°C the reaction mixture was decomposed with 1% sulfuric acid at 0°C. The ether layer was dried with calcium chloride, and the solvent distilled at the water pump. The residue 8.4 g, 90% was an oily liquid. Found: C 41.93; 41.98; H 4.82; 4.89%. $C_{13}H_{18}Hg$. Calculated: C 41.65; H 4.84%.

* In this way symmetric organomercury compounds are converted into asymmetric compounds containing an acetyl group, which are soluble in dilute acetic acid.

Results of the Reactions of Asymmetric and Symmetric Organomercury Compounds with Carbon Tetrachloride in the Presence of Benzoyl Peroxide

No.	Starting compounds		Quantity, g	Reaction time, hr	Reaction products		
	Formula	Constants			Formula	m.p., °C	Quantity, %
1	$C_6H_5HgC_2H_5$ $(C_6H_5COO)_2$ CCl_4	Liquid	11,4 0,8 70 ml	6	C_6H_5HgCl C_6H_5COOH $CCl_3—CCl_3$ $1—Cl—2,4(NO_2)_2C_6H_3$	190—191 121 185 52	86,7
2	$C_4H_9HgC_6H_5$ $(C_6H_5COO)_2$ CCl_4	Liquid	5.00 0,6 25 ml	8	C_4H_9HgCl C_6H_5COOH $CCl_3—CCl_3$	128—130 116—118 178—183	76 72 —
3	$C_4H_9HgCH_2C_6H_5$ $(C_6H_5COO)_2$ CCl_4	Liquid	5,22 0,8 25 ml	6	$C_6H_5CH_2HgCl$ $C_4H_9CCl_3$	100—102 b.p. 77° (54 mm) n_D^{20} 1,4560	73 58
4	$C_4H_9HgC_2H_5$ $(C_6H_5COO)_2$ CCl_4	Liquid	5,72 0,6 45 ml	7	C_4H_9HgCl $C_2H_5CCl_3$ Hg	126—129 b.p. 35° (60 mm n_D^{20} 1,4502	70 20 18
5	$C_6H_5CH_2HgC_6H_5$ $(C_6H_5COO)_2$ CCl_4	Liquid	7,3 0,8 50 ml	6	$C_6H_5CH_2HgCl$ C_6H_5COOH C_6H_5HgCl Hg	99—101 120 250	73,4 33 — 2,5
6	$C_6H_5HgC_6H_{11}$ $(C_6H_5COO)_2$ CCl_4	m.p., °C 59—61°	5,4 0.55 25 ml	8,5	$C_6H_{11}HgCl$ C_6H_5COOH Hg	161—162 120 —	80,7 43 —
7	$C_4H_9HgC_6H_{11}$ $(C_6H_5COO)_2$ CCl_4	Liquid	6,8 0,7 50 ml	7	$C_6H_{11}HgCl$ $(C_6H_{11})_2Hg$ $C_4H_9CCl_3$ Hg	155—157 b.p. 68° (53 mm) n_D^{20} 1,4562	84,6 — 60,5 —

TABLE (Continued)

No.	Starting compounds		Quantity, g	Reaction time, hr	Reaction products		
	Formula	Constants			Formula	m.p., °C	Quantity, %
8	$C_6H_5CH_2HgC_6H_{11}$ $(C_6H_5COO)_2$ CCl_4	Liquid	4,8 0,55 40 ml	8	$C_6H_{11}HgCl$ $C_6H_5CH_2HgCl$ $C_6H_5CH_2COOH$ $C_6H_{11}COOH$	~153—155 98—100 74— 75 28 m.p. °C 72° (1 mm)	60 17 42 12,5
9	$C_6H_5HgC_6H_2(CH_3)_3$ $(C_6H_5COO)_2$ CCl_4	m.p., °C 145—149°	3,9 0,4 40 ml	6	C_6H_5HgCl $(CH_3)_3C_6H_2COOH$	249—251 154—156	93,6 30,7
10	α-$C_{10}H_7HgC_6H_2(CH_3)_3$ $(C_6H_5COO)_2$ CCl_4	m.p., °C 177—179°	4,4 0,5 40 ml	7	α-$C_{10}H_7HgCl$ $(CH_3)_3C_6H_2COOH$	183—186 150—152	73 36
11	α-$C_{10}H_7HgC_6H_5$ $(C_6H_5COO)_2$ CCl_4	m.p., °C 165—195°	5,8 1,0 80 ml	8	C_6H_5HgCl α-$C_{10}H_7COOH$ CCl_3—CCl_3 1—Cl—2,4$(NO_2)_2C_6H_3$	251 160—161 185 51	85,2 73,1 — —
12	p-$CH_3C_6H_4HgC_6H_5$ $(C_6H_5COO)_2$ CCl_4	m.p., °C 167—192°	4,2 0,8 60 ml	8	C_6H_5HgCl p-$CH_3C_6H_4COOH$ CCl_3—CCl_3 1—Cl—2,5$(NO_2)_2C_6H_3$	251 178—179 185 51	88,6 82 —
13	o-$CH_3C_6H_4HgC_6H_4CH_3$-p $(C_6H_5COO)_2$ CCl_4	m.p. °C 159—189°	4,5 0,8 85 ml	7	o-$CH_3C_6H_4HgCl$ p-$CH_3C_6H_4HgCl$ o-$CH_3C_6H_4COOH$ p-$CH_3C_6H_4COOH$ o-$CH_3C_6H_4HgCl$: p-$CH_3C_6H_4HgCl$-53 : 47 o-$CH_3C_6H_4COOH$: p-$CH_3C_6H_4COOH$-40 : 60	140—142 230—232 102 177—179	91 62,5
14	o-$CH_3C_6H_4Hg$-$C_6H_4CH_3$-m $(C_6H_5COO)_2$ CCl_4	m.p. °C 92—97°	2,0 0,2 40 ml	6	m-$CH_3C_6H_4HgCl$ o-$CH_3C_6H_4HgCl$ o-$CH_3C_6H_4COOH$	158—159 140—142 101	69,5 8,7

TABLE (Continued)

No.	Starting compounds		Quantity, g	Reaction time, hr	Reaction products		
	Formula	Constants			Formula	m.p., °C	Quantity %
15	$(p\text{-}CH_3C_6H_4)_2Hg$ + $+(m\text{-}CH_3C_6H_4)_2Hg$ $(C_6H_5COO)_2$ CCl_4	m.p., °C 235° 99—100°	2.0 2.0 0,4 200 ml	3	$(m\text{-}CH_3C_6H_4)_2Hg$ $m\text{-}CH_3C_6H_4HgCl$ $p\text{-}CH_3C_6H_4HgCl$ $(p\text{-}CH_3C_6H_4)_2Hg$ $p\text{-}CH_3C_6H_4COOH$ $m\text{-}CH_3C_6H_4COOH$	99—100 157—159 230 235 175—176 107—108	55 29,2 46,6 40
16	$(m\text{-}CH_3C_6H_4)_2Hg$ + $+(\alpha\text{-}C_{10}H_7)_2Hg$ $(C_6H_5COO)_2$ CCl_4	m.p. °C 99—100° 249°	2,38 2,00 0,4 250ml	3,5	$m\text{-}CH_3C_6H_4HgCl$ $\alpha\text{-}C_{10}H_7HgCl$ $\alpha\text{-}C_{10}H_7COOH$ $m\text{-}CH_3C_6H_4COOH$ $m\text{-}CH_3C_6H_4HgCl$	158—159 188—189 159—161 103—109 158—159	49,5 82 30,5 *
17	$(o\text{-}CH_3C_6H_4)_2Hg$ + $+(\alpha\text{-}C_{10}H_7)_2Hg$ $(C_6H_5COO)_2$ CCl_4	m.p. °C 107° 249°	2,00 2,38 0,4 200 ml	1,5	$o\text{-}CH_3C_6H_4HgCl$ $\alpha\text{-}C_{10}H_7HgCl$ $\alpha\text{-}C_{10}H_7COOH$ $o\text{-}CH_3C_6H_4HgCl$	142 187—188 159—161 142	6 85 — 79,2*
18	$(m\text{-}CH_3C_6H_4)_2Hg$ + $(C_6H_5)_2Hg$ $(C_6H_5COO)_2$ CCl_4	m.p. °C 99—100° 124°	2,0 1,85 0,4 200 ml	2	$m\text{-}CH_3C_6H_4HgCl$ C_6H_5HgCl $m\text{-}CH_3C_6H_4COOH$ C_6H_5HgCl	157—158 248—250 109 250	84 11 70*
19	$(\alpha\text{-}C_{10}H_7)_2Hg$ + $+(p\text{-}CH_3C_6H_4)_2Hg$ $(C_6H_5COO)_2$ CCl_4	m.p., °C 249° 235°	2,38 2,00 0,4 200 ml	1	$\alpha\text{-}C_{10}H_7HgCl$ $n\text{-}CH_3C_6H_4HgCl$ $\alpha\text{-}C_{10}H_7COOH$ $n\text{-}CH_3C_6H_4COOH$ $\alpha\text{-}C_{10}H_7HgCl$ $p\text{-}CH_3C_6H_4HgCl$	167—168 230 159—161 176 186—187 232	47,4 36,5 36,8* 48,7*

* Organomercury chlorides separated after decomposition with acetic acid of the R_2Hg not consumed in the reaction, and precipitation with NaCl.

Ethyl-n-butylmercury. Finely powdered butylmercury bromide (16.88 g 0.05 M) was added in small portions at 2-10°C to a vigorously stirred solution of the Grignard reagent prepared from 10.9 g (0.1 M) ethyl bromide and 2.4 g (0.1 M) magnesium in 45 ml dry ether. After 2 hours the reaction mixture was decomposed with 100 ml 1% sulfuric acid at 5°C. After drying the ether layer with calcium chloride the solvent was evaporated at the water pump. The residue 13 g (90%) was a mobile liquid, $n_D^{21.5}$ 1.5114. Found: C 25.54; 25.53; H 5.06; 5.03; Hg 69.72; 69.71%. $C_6H_{14}Hg$. Calculated: C 25.12; H 4.92; Hg 69.97%.

α-Naphthylmesitylmercury. Finely powdered α-naphthylmercury bromide (5.1 g, 0.0125 M) was added at room temperature to the Grignard reagent prepared from 5 g (0.025 M) bromomesitylene and 0.6 g (0.025 M) magnesium in 35 ml dry ether. After 1.5 hours stirring at 30-35°C the reaction mass was decomposed with 1% sulfuric acid at 5-10°C. A crystalline substance (3.7 g, 83%) with m.p. 177-179°C was obtained. Found: C 50.83; 50.67; H 4.06; 4.13; Hg 44.74; 44.55%. $C_{19}H_{18}Hg$. Calculated: C51.06; H 4.06; Hg 44.89%.

Butylbenzylmercury. Benzylmercury chloride (16.36 g, 0.05 M) was added in small portions to a stirred solution of the Grignard reagent prepared from 2.4 g (0.1 M) magnesium and 14.0 g (0.1 M) butyl bromide in 50 ml dry ether. The reaction mixture was heated at 34-40°C or 20 min, and then cooled and decomposed with 1% sulphuric acid. The ether layer was separated and dried over calcium chloride. After complete separation of the ether 15.4 g (88%) of a liquid substance was obtained. Found: C 37.37; 37.24; H 4.51; 4.51%. $C_{11}H_{16}Hg$. Calculated: C 34.58; H 4.62%.

Phenylbenzylmercury. Benzylmercury chloride (16.35 g, 0.05 M) was added at 4-6°C to a Grignard solution prepared from 2.4 g (0.1 M) magnesium and 15.7 g (0.1 M) bromobenzene in 75 ml dry ether. The reaction product was decomposed with 1% sulfuric acid. The ether layer was separated and dried over calcium chloride. After complete removal of the solvent 7.25 g (39%) of a liquid, which appeared slightly colored in yellow light, was obtained. Found: C 42.25; 42.24; H 3.27; 3.08%. $C_{13}H_{12}Hg$. Calculated: C 42.33; H 3.28%.

Butylcylohexylmercury. Cyclohexylmercury bromide (9.09 g, 0.025 M) was added at 0-6°C to a solution prepared from 1.2 g (0.05 M) magnesium and 6.85 g (0.05 M) butyl bromide in 75 ml dry ether. After stirring for 1 hr the reaction product was decomposed with 1% sulfuric acid, the ether layer separated and dried over calcium chloride. The solvent was removed completely at the water pump. The product (7.8 g, 92%) was a slightly colored liquid. Found: C 35.19; 35.22, H 5.80; 5.95; Hg 58.94; 58.64%. $C_{10}H_{20}Hg$. Calculated: C 35.20; H 5.92; Hg 58.98%.

SUMMARY

1. The reaction of asymmetric organomercury compounds with carbon tetrachloride proceeds via a radical mechanism in the presence of benzoyl peroxide. The less reactive group linked to mercury in RHgR' stays attached to mercury, but the more reactive group is converted into $RCCl_3$.

2. A series has been established for radicals arranged in order of decreasing affinity towards the free radical CCl_3.

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REACTIONS OF HALOGEN REPLACEMENT OF A MERCURY ATOM CONNECTED TO A SATURATED CARBON ATOM

COMMUNICATION 1. INTERACTION OF BENZYLMERCURY CHLORIDE WITH IODINE, IN THE PRESENCE OF IODIDE ION, IN DIOXANE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1589-1595, September, 1961
Original article submitted January 19, 1961

In a series of studies directed toward the investigation of the mechanism of electrophilic substitution at a saturated carbon atom in organomercury compounds, we have investigated the reaction of benzylmercury chloride with iodine in the presence of a large excess of iodide ion *

$$C_6H_5CH_2HgCl + I_2(CdI_2) \rightarrow C_6H_5CH_2I + HgClI + CdI_2$$

As the source of iodide ions we used cadmium iodide, since the iodides of Group I elements usually applied for this purpose "symmetrize" the benzylmercury chloride to dibenzylmercury. It was demonstrated by special experiments that under our conditions the reaction proceeds with quantitative formation of benzyl iodide, and that the inorganic mercury salt HgClI formed in the reaction does not change the concentration of the reacting iodine and does not interfere with its determination. The kinetics of the reaction were measured by two methods: titrometrically and spectrophotometrically. In the first case the reaction was carried out over the range of reactant concentrations $(2.4\text{-}4.8)\cdot 10^{-3}$ mole/liter and cadmium iodide concentration approximately 0.05 mole/liter.

EXPERIMENTAL

To a thermostated solution of benzylmercury chloride in dioxane**, a water–dioxane solution of iodine and cadmium iodide (preheated to the same temperature) was added with stirring. The ratio of dioxane and water corresponded to a 70% solution. The temperature of the experiment was controlled to ± 0.1°C. The moment of adding the second reactant was taken as the start of the reaction. At definite time intervals, 1 ml of the reaction mixture was withdrawn and back-titrated with sodium thiosulfate solution. The reaction rate constant was calculated by the second-order reaction equation

$$K_2 = \frac{2.303}{\tau(a-b)}\log\frac{b(a-x)}{a(b-x)}$$

The reaction kinetics were studied at 15, 20, 24, and 25°C.

Table 1 shows values of the second-order reaction rate constant obtained both for equimolar and for differing initial reactant concentrations, and also values of the constants obtained on varying the temperatures.

Plots on the coordinates

$$\frac{1}{a-b}\log\frac{b(a-x)}{a(b-x)} - \tau \text{ and } \frac{x}{a-x} - \tau$$

* It was shown previously by Winstein [1] that the presence of iodide under these conditions ensures that the reaction will proceed by an electrophilic route, and suppresses the radical substitution mechanism.
** The dioxane was freed of peroxides by the method of Mitchell and Smith [2].

TABLE 1.

Expt. 1. $[C_6H_5CH_2HgCl] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[I_2] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[Na_2S_2O_3] = 4.951 \cdot 10^{-3}$ mole/liter; t = 20°C

τ, sec	Quantity thiosulfate, ml	$\frac{x}{a-x}$	$K_2 \cdot 10$ liters/mole · sec
240	1,34	0,435	3,80
420	1,06	0,800	4,00
600	0,94	1,038	3,87
845	0,75	1,558	3,88
1035	0,66	1,880	3,80
1260	0,64	1,970	3,28
		Average	0,377

Expt. 2. $[C_6H_5CH_2HgCl] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[I_2] = b = 4.737 \cdot 10^{-3}$ mole/liter; $[Na_2S_2O_3] = 9.569 \cdot 10^{-4}$ mole/liter; t = 20°C

τ, sec	Quantity of thiosulfate, ml	$(b-x) \cdot 10^3$	$\lg \frac{b(a-x)}{a(b-x)}$	$K_2 \cdot 10$, liters/mole · sec
120	8,10	3,875	0,0005	3,43
280	6,37	3,047	0,0013	3,82
480	5,28	2,526	0,0022	3,78
660	4,42	2,114	0,0031	3,86
1100	3,62	1,731	0,0044	3,28
			Average	0,365

Expt. 3 *. $[C_6H_5CH_2HgCl] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[I_2] = b = 4.737 \cdot 10^{-3}$ mole/liter; $[Na_2S_2O_3] = 9.569 \cdot 10^{-4}$ mole/liter; t = 20°C

τ, sec	Quantity of thiosulfate, ml	$(b-x) \cdot 10^3$	$\lg \frac{b(a-x)}{a(b-x)}$	$K_2 \cdot 10$, liters/mole · sec
480	5,45	2,607	0,0021	3,61
700	4,51	2,157	0,0031	3,65
840	4,04	1,933	0,0036	3,52
1060	3,61	1,726	0,0044	3,42
			Average	0,355

Expt. 4. $[C_6H_5CH_2HgCl] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[I_2] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[Na_2S_2O_3] = 9.903 \cdot 10^{-4}$ mole/liter; t = 24°C

τ, sec	Quantity of thiosulfate, ml	$\frac{x}{a-x}$	$K_2 \cdot 10$, liters/mole · sec
90	7,85	0 210	4,90
240	5,99	0,600	5,25
400	5,01	0,915	4,80
525	4,14	1,320	5,28
680	3,72	1,572	4,89
900	3,27	1,923	4,50
1080	2,69	2,550	4,97
		Average	0,480

* Experiment 3 is a reproducibility check on Experiment 2.

Expt. 5. $[C_6H_5CH_2HgCl] = a = 2.382 \cdot 10^{-3}$ mole/liter; $[I_2] = b = 2.376 \cdot 10^{-3}$ mole/liter; $[Na_2S_2O_3] = 4.951 \cdot 10^{-4}$ mole/liter t = 24°C

τ, sec	Quantity of thiosulfate, ml	$(b-x) \cdot 10^3$	$\lg \frac{b(a-x)}{a(b-x)}$	$K_2 \cdot 10$, liters/mole · sec
85	8,58	2,124	0,0001	4,51
305	6,57	1,626	0,0004	5,03
380	6,12	1,515	0,0005	5,05
510	5,94	1,470	0,0006	4,51
605	5,19	1,284	0,0008	5,08
740	4,68	1,158	0,0011	5,71
880	4,38	1,084	0,0012	5,23
925	4,20	1,039	0,0013	5,39
1080	3,82	0,945	0,0016	5,68
1115	3,80	0,940	0,0016	5,65
1290	3,44	0,851	0,0019	5,56
			Average	0,521

Expt. 6. $[C_6H_5CH_2HgCl] = a = 4.765 \cdot 10^{-3}$ mole/liter $[I_2] = b = 2.376 \cdot 10^{-3}$ mole/liter; $[Na_2S_2O_3] = 4.951 \cdot 10^{-4}$ mole/liter; t = 24°C

τ, sec	Quantity of thiosulfate, ml	$(b-x) \cdot 10^3$	$\lg \frac{b'a-x)}{a,b-x)}$	$K_2 \cdot 10$, liters/mole · sec
105	7,48	1,851	0,0566	5,20
270	5,35	1,325	0,1454	5,20
405	3,99	0,9875	0,3316	4,46
525	3,50	0,8665	0,3862	5,65
660	2,81	0,6955	0 3446	5,37
840	2,16	0,5345	0,4359	5,04
975	2,01	0,4975	0,4612	5,00
			Average	0,509

TABLE 1 (Continued)

Expt. 7. $[C_6H_5CH_2HgCl] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[I_2] = b = 4.737^{-3}$ mole/liter $[Na_2S_2O_3] = 9.569 \cdot 10^{-4}$ mole/liter; t = 15°C

τ, sec	Quantity of thiosulfate, ml	$(b-x) \cdot 10^3$	$\lg \frac{b'a-x)}{a(b-x)}$	$K_2 \cdot 10$, liters/mole · sec
295	7,13	3,411	0,0009	2,50
315	7,09	3,391	0,0010	2,61
495	5,86	2,803	0,0017	2,83
700	5,14	2,459	0,0023	2,70
730	4,68	2,237	0,0028	3,16
960	4,61	2,205	0,0029	2,50
1210	4,13	1,976	0,0034	2,37
1260	3,81	1,824	0,0041	2,68
1510	3,48	1,574	0,0050	2,72
			Average	0,245

Expt. 8. $[C_6H_5CH_2HgCl] = a = 4.765 \cdot 10^{-3}$ mole/liter; $[I_2] = b = 4.737 \cdot 10^{-3}$ mole/liter; $[Na_2S_2O_3] = 9.569 \cdot 10^{-4}$ mole/liter; t = 25°C

τ, sec	Quantity of thiosulfate, ml	$(b-x) \cdot 10^3$	$\lg \frac{b(a-x)}{a(b-x)}$	$K_2 \cdot 10$, liters/mole · sec
120	7,59	3,630	0,0008	5,50
270	5,73	2,741	0,0017	6,53
325	5,23	2,501	0,0023	5,83
390	4,65	2,224	0,0028	5,92
480	4,19	2,004	0,0035	6,00
580	3,87	1,851	0,0039	5,54
690	3,61	1,726	0,0044	5,25
810	3,24	1,549	0,0051	5,20
910	3,14	1,502	0,0067	6,06
1100	2,90	1,387	0,0074	5,54
1230	2,59	1,239	0,0084	5,62
			Average	0,563

(Figs. 1-6) demonstrate the convergence in the values of the second order rate constants for the cases of differing initial concentrations of benzylmercury chloride and iodine, with temperature constant (and the changes in the values of these constants on variation of temperatures). From the plots of Figs. 1-6, average values of the reaction rate constants were found graphically.

TABLE 2.

K_2, liters/mole · sec	log K_2	τ	$\frac{1}{\tau} \cdot 10^4$
0.30	−0.5229	288	34.7
0.37	−0.4318	293	34.1
0.48	−0.3188	297	33.6
0.58	−0.2366	298	33.5

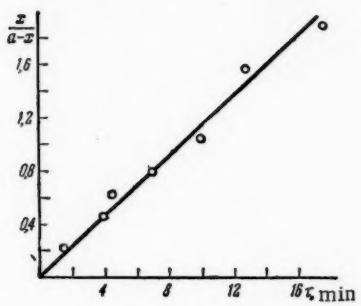

Fig. 1. x/(a-x) vs. τ, Experiment 1.

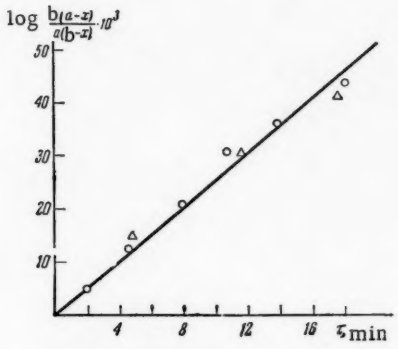

Fig. 2. log $\frac{b(a-x)}{a(b-x)} \cdot 10^3$ vs. τ, Experiments 2 (O) and 3 (Δ).

Table 2 shows values of the second-order reaction rate constants obtained at different temperatures, their logarithms, the corresponding absolute temperatures, and their reciprocals.

The dependence of the logarithm of the reaction rate constant on reciprocal temperature is shown in Fig. 7. From this plot the following parameters of the Arrhenius equation are found: E = 10.8 kcal/mole; log A = 7.7. The entropy of activation Δ S = -23.3 entropy units at 20°C.

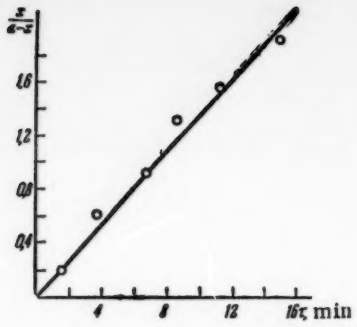

Fig. 3. x/(a-x) vs. τ, Experiment 4.

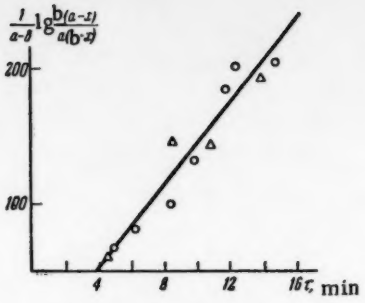

Fig. 4. $\frac{1}{a-b} \log \frac{b(a-x)}{a(b-x)} \cdot 10^3$ vs. τ, Experiments 5 and 6.

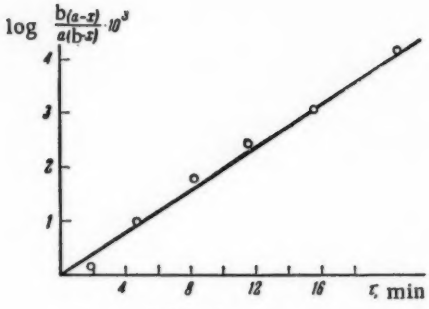

Fig. 5. $\log \frac{b(a-x)}{a(b-x)} \cdot 10^3$ or τ, Experiment 7.

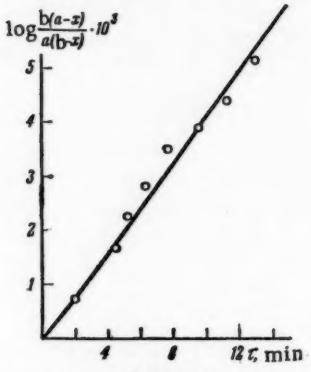

Fig. 6. $\log \frac{b(a-x)}{a(b-x)} \cdot 10^3$ vs. τ, Experiment 8.

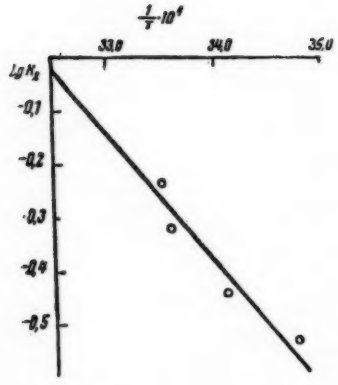

Fig. 7. $\log K_2$ vs $\frac{I}{T} \cdot 10^4$, for Table 2.

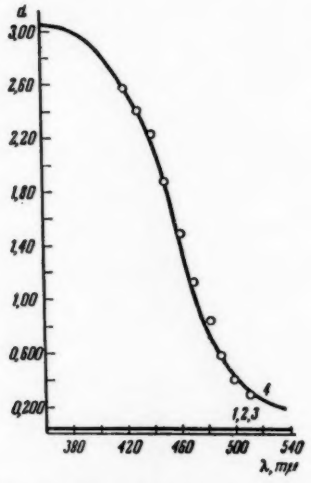

Fig. 8. Optical density as a function of wavelength for: 1) dioxane, 2) $C_6H_5CH_2HgCl$, 3) $C_6H_5CH_2I + CdI_2 +$ + HgICl, and 4) $I_2 + CdI_2 + CdI_2$.

Experiment 1. $c_0 = 8.34 \cdot 10^{-4}$ mole/liter

τ, sec	d	$c \cdot 10^4$ moles/liter	$K_2 \cdot 10$, liters/mole · sec
198	0,740	7,74	4,70
318	0,700	7,33	5,24
397	0,672	7,03	5,68
477	0,649	6,79	5,74
636	0,610	6,40	5,73
792	0,572	6,10	5,56
990	0,533	5,60	5,92
1191	0,502	5,26	5,86
1350	0,478	5,03	5,86
1524	0,449	4,72	5,80
1811	0,420	4,42	5,85
2060	0,398	4,17	5,81
2379	0,373	3,95	5,58
2618	0,356	3,76	5,58
2850	0,340	3,56	5,64
3118	0,325	3,40	5,58
3330	0,314	3,30	5,51
3560	0,302	3,20	5,36
3962	0,285	3,00	5,36
4200	0,278	2,90	5,24
4440	0,269	2,80	5,36
4750	0,260	2,74	5,14
		Average	0,580

Experiment 2.• $c_0 = 8.34 \cdot 10^{-4}$ mole/liter

τ, sec	d	$c \cdot 10^4$ moles/liter	$K_2 \cdot 10$, liters/mole · sec
159	0,759	7,92	3,94
238	0,728	7,60	4,87
397	0,678	7,08	5,36
476	0,650	6,80	5,74
635	0,606	6,45	5,52
795	0,574	6,00	5,88
955	0,544	5,70	5,80
1112	0,518	5,42	5,80
1352	0,480	5,08	5,70
1510	0,459	4,80	5,86
1590	0,450	4,75	5,71
1750	0,427	4,50	5,85
1979	0,411	4,32	5,64
2225	0,385	4,05	5,70
2304	0,375	3,95	5,59
2654	0,351	3,66	5,75
2861	0,343	3,60	5,51
3100	0,326	3,40	5,64
3340	0,315	3,30	5,49
3580	0,303	3,20	5,37
3818	0,293	3,10	5,34
4060	0,284	2,98	5,34
		Average	0,580

• Experiment 2 was made to study reproducibility.

Experiment 3. $c = 4.17 \cdot 10^{-4}$ mole/liter

τ, sec	d	$c \cdot 10^4$ moles/liter	$K_2 \cdot 10$, liters/mole · sec
192	0,382	4,01	5,01
287	0,376	3,97	4,18
480	0,359	3,78	5,03
766	0,338	3,51	5,90
958	0,326	3,40	5,66
1435	0,296	3,10	5,76
1919	0,273	2,88	5,62
2395	0,253	2,68	5,56
2874	0,238	2,48	5,68
3355	0,224	2,35	5,52
3835	0,211	2,22	5,51
4318	0,200	2,13	5,34
4780	0,189	1,98	5,54
5260	0,181	1,90	5,44
5750	0,174	1,80	5,51
6900	0,159	1,67	5,21
7379	0,154	1,61	5,17
7663	0,150	1,56	5,22
8445	0,143	1,50	5,05
9015	0,138	1,46	4,94
9595	0,133	1,40	4,96
		Average	0,550

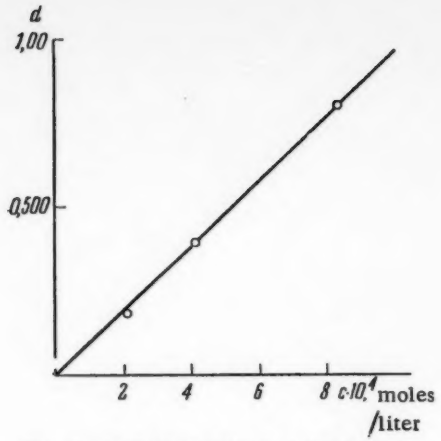

Fig. 9. Optical density as a function of I_2 concentration in the presence of CdI_2.

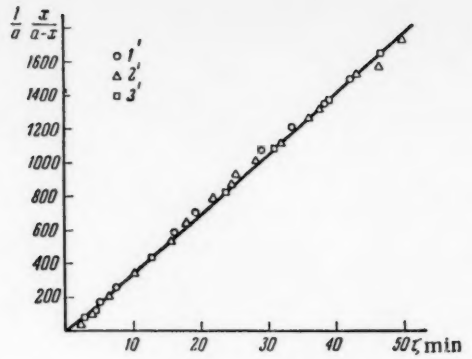

Fig. 10. $\frac{1}{a}\ \frac{x}{a-x}$ vs. τ in Experiments 1', 2', and 3'.

In the second case, the reaction kinetics were taken spectrophotometrically with equimolar concentrations of the benzylmercury chloride and iodine ($4.17 \cdot 10^{-4}$ and $8.34 \cdot 10^{-4}$ mole/liter) and a tenfold excess of cadmium iodide. The reaction temperature was 25 ± 1°C. The optical density of the solution was measured at 470 mμ. Fig. 8 shows the function $d = f(\lambda)$ in dioxane for benzylmercury chloride, benzyl iodide in the presence of mercury iodochloride and cadmium iodide, and iodine in the presence of cadmium iodide.

Fig. 9 shows the calibration curve for the optical density d as a function of the concentration of iodine in 70% dioxane solution containing cadmium iodide.

The experimental data on the change in optical density of the solution during the reaction are summarized in Table 3. The reaction rate constant satisfies the equation for biomolecular reactions

$K_2 = \frac{1}{a\tau}\left(\frac{a}{a-x} - 1\right)$. The plot on coordinates $\left[\frac{1}{a}\ \frac{x}{(a-x)}\right]$ vs. τ (Fig. 10) illustrates the good convergence in the values of second-order reaction rate constants determined spectrophotometrically. This value, $K_2 = 0.570$ liter/mole · sec, shows sufficiently good agreement with the value of K_2 found titrometrically at 25°C.

SUMMARY

1. A study has been made of the electrophilic replacement of mercury by iodine in benzylmercury chloride.

2. The reaction kinetics have been measured by two methods: spectrophotometrically and titrometrically.

3. The reaction of benzylmercury chloride with iodine in the presence of cadmium iodide in 70% aqueous dioxane is second order over-all, and first order with respect to each of the components.

4. The parameters of the Arrhenius equation have been determined: E = 10.8 kcal/mole, log A = 7.7, and entropy of activation $\Delta S = -23.3$ entropy units at 20°.

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DISPROPORTIONATION REACTIONS OF ORGANIC COMPOUNDS CONTAINING ZIRCONIUM, TITANIUM, AND IRON

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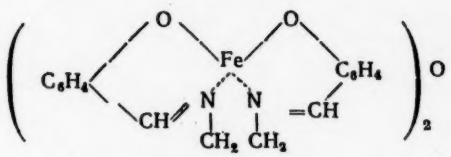
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1595-1599, September, 1961
Original article submitted February 21, 1961

For the titanium subgroup elements there has been little study of compounds containing element–oxygen–element chains. In the case of titanium, certain low molecular weight individual compounds of the titanoxane type have been prepared [1]. There are known both fully alkoxylated hexaalkoxydititanoxanes [2, 3] and octaalkoxytrititanoxanes [4, 5] and mixed alkoxytrititanoxanes containing halogen [5], and also hexaacyloxydititanoxanes [6]. Organic compounds containing zirconoxane groups -Zr-O-Zr- are almost unknown. It is reported in the literature [7] that on the interaction of fatty acids with tetraisopropoxyzirconium there are formed hexaacyloxydizirconoxanes of the composition: $(RCO_2)_3Zr-O-Zr(CO_2R)_3$, where R = C_9H_{19}, $C_{11}H_{23}$, $C_{15}H_{31}$, and $C_{17}H_{35}$. As regards the analogous iron compounds, there is a communication [8] in the literature on the preparation of a compound having the following structure:



In the present article we describe the preparation in pure form of crystalline tetraacetoxytetraethoxytrititanoxane $(C_2H_5O)_4(CH_3CO_2)_4Ti_3O_2$, by the interaction of acetic anhydride with tetraethoxytitanium in 2:1 molar ratio, under conditions eliminating the access of moisture from the air. One of the routes to the formation of organic zirconoxane compounds could prove to be hydrolysis of zirconium alkoxides. We investigated the interaction of water with tetrabutoxyzirconium with definite molar ratios corresponding to the following equation:

$$n(C_4H_9O)_4Zr + (n-1)H_2O \rightarrow (C_4H_9O)_{2n+2}Zr_nO_{n-1} + 2(n-1)C_4H_9OH \quad (1)$$

This interaction yielded semisolid substances, readily soluble in the usual organic solvents and decomposing on distillation under high vacuum. The hydrolysis products, after freeing from traces of butanol by vacuum drying, were analyzed for C, H, and Zr. The analytical results are shown in the table.

For $(C_4H_9O)_6Zr_2O$, the molecular weight found was 600-650, vs. 636 calculated. The molecular weight determination was made cryoscopically in benzene; however, the reproducibility was poor, since the benzene solutions of all of the obtained hydrolysis products became turbid in several hours.

It might be expected that the interaction of the products with β-diketones would lead to clathrate compounds containing -Zr-O-Zr- groups. However, on the action of acetylacetone or benzoylacetone on the "dimer" or "trimer"*, zirconium tetraacetylacetonate or tetrabenzoylacetonate is formed.

*Here and later in the article, we use the terms "dimer" and "trimer" to designate the hydrolysis products described in the table.

The reaction may be described by the scheme:

$$A.\ (C_4H_9O)_6Zr_2O + 6C_5H_8O_2 \rightarrow (C_5H_7O_2)_6Zr_2O + 6C_4H_9OH$$

$$B.\ (C_5H_7O_2)_6Zr_2O \rightarrow (C_5H_7O_2)_4Zr + (C_5H_7O_2)_2ZrO$$

$$C.\ (C_5H_7O_2)_2ZrO + 2C_5H_8O_2 \rightarrow (C_5H_7O_2)_4Zr + H_2O$$

For simplification of the scheme, it is assumed that in stage A there is complete exchange of the alkoxyl groups, and in stage B disproportionation of the completely substituted zirconoxane. The final stage C is analogous to the process occurring in the formation of zirconium diacetylacetonate dinitrate from zirconyl nitrate and acetylacetone [9].

$$(NO_3)_2ZrO + 2C_5H_8O_2 - (NO_3)_2Zr(C_5H_7O_2)_2 + H_2O$$

In this connection it is interesting to note that the hydrolysis of crystalline zirconium isopropoxytriacetylacetonate likewise does not go to the formation of the dimer:

$$2i\text{-}C_3H_7OZr(C_5H_7O_2)_3 \xrightarrow{H_2O} (C_5H_7O_2)_6Zr_2O + 2C_3H_7OH;$$

but as the main product of hydrolysis forms zirconium tetraacetylacetonate, possibly as a result of disproportionation by a scheme analogous to B. Zirconium triacetylacetonate chloride, zirconium tribenzoylacetonate nitrate, and the chlorides of the diacetyl- and dibenzoylacetonates of iron undergo a similar disproportionation process under the influence of water. It should be noted that a phenomenon of the same nature was observed by Nogina on the interaction of acetylacetone with octaethoxytrititanoxane. Instead of the expected trimer, containing clathrate groups, compounds were obtained by the following scheme:

$$(C_2H_5O)_3Ti{-}O{-}\cdots{-}TiO(OC_2H_5) \cdots Ti(OC_2H_5)_3 + 6CH_3COCH_2COCH_3 \rightarrow$$

$$\rightarrow (C_2H_5O)_2\,Ti(C_5H_7O_2)_2 + 2(C_5H_7O_2)_2\,Ti\,O + 6C_2H_5OH$$

Zirconium isopropoxytriacetylacetonate and zirconium tri-n-propoxyacetylacetonate were obtained by the interaction of zirconium tetraacetylacetonate with the corresponding alcohols.

EXPERIMENTAL

Interaction of Tetrabutoxyzirconium with Water in 2:1 Molar Ratio. To a solution of 6.35 g (0.016 mole) of tetrabutoxyzirconium in 5 ml of butanol, there was added gradually with vigorous stirring 0.148 ml (0.008 mole) of water and 2 ml of butanol, at 60°C. Then the temperature of the mixture was raised to 110°C, and stirring was continued 20 minutes. The reaction mixture was filtered off from the flasks which were formed (0.12 g). The solvent was distilled from the filtrate. The residue was freed from traces of butanol at 90°C and 1 mm. Obtained a semisolid mass, very readily soluble in benzene, chloroform, petroleum ether, and other organic solvents, from which the resulting product could not be recrystallized successfully. Found: C 45.38; 45.37; H 8.66; 8.58; Zr 28.44; 28.49%. $(C_4H_9O)_6Zr_2O$. Calculated: C 45.22; H 8.55; Zr 28.64%.

Experiments were conducted analogously with 3:2, 4:3, and 10:9 molar ratios of tetrabutoxyzirconium and water. The results obtained are summarized in the table.

Action of Acetylacetone and Benzoylacetone on "Dimer" and "Trimer." A mixture of "dimer" (2.15 g) and 10 ml of acetylacetone was heated to 130-140°C, with the pressure reduced for distilling off the butanol. In 30 minutes the separation of crystals began; weight of the dry residue was 2.8 g (85% of theoretical)*, m.p. 190-194°C. The recrystallized product melted at 191-194° and did not show any melting-point depression in mixture with zirconium acetylacetonate.

A mixture of molten benzoylacetone 3.02 g (0.018 mole) and "dimer" 2 g (0.0031 mole) was heated for 10 minutes at 70°C. Benzene was added to the reaction mass, and the crystalline residue which was precipitated was

*Considering that the weight of the zirconium contained in the starting material is found in the final mixture in the form of zirconium tetraacetylacetonate or tetrabenzoylacetonate.

filtered off, washed with hot benzene and with petroleum ether, and dried for one hour on the filter. Obtained 2.35 g (58% of theoretical)* of a substance, m. p. 207-210°C, unchanged after recrystallization, and giving no melting-point depression in a mixed sample with zirconium benzoylacetonate.

A solution of 3 g of the "trimer" in petroleum ether was added to 11 ml of acetylacetone. On shaking the reaction mixture, the separation of a crystalline sediment began at room temperature. Obtained a total of 4.18 g (84% of theoretical) of zirconium tetraacetylacetonate.

Action of Water on Zirconium Triacetylacetonate Chloride. Zirconium triacetylacetonate chloride (2 g) was dissolved in 4 ml of distilled water. The residue, which precipitated immediately, was filtered off; it represented zirconium tetraacetylacetonate. Yield 60% of theoretical, based on the equation:

$$2(C_5H_7O_2)_3ZrCl + H_2O \rightarrow (C_5H_7O_2)_4Zr + ZrOCl_2 + 2C_5H_8O_2$$

Analogously, from zirconium tribenzoylacetonate mononitrate and water, obtained zirconium tetrabenzoylacetonate with 54% yield.

Zirconium Isopropoxytriacetylacetonate. Zirconium tetraacetylacetonate (8.2 g) was dissolved with heating in excess isopropanol (45 ml). Distillation of the mixture of acetylacetone and isopropanol was effected at 94°C in a stream of dry air. After many repetitions of this procedure, acetylacetone was no longer detected in the distillate; however, the reaction mixture gave a positive test with $FeCl_3$ for the presence of acetylacetone. After distilling off the volatile products at 45°C and 1 mm, a light-colored crystalline powder was obtained. The product was recrystallized from isopropanol, washed with petroleum ether, and dried for one hour on the filter; m.p. 183-184°C. Found: C 47.74; 48.05; H 6.19; 6.10; Zr 20.49; 20.82%. $i\text{-}C_3H_7OZr(C_5H_7O_2)_3$. Calculated: C 48.27; H 6.30; Zr 20.39%. On the action of water on the obtained zirconium isopropoxytriacetylacetonate, zirconium tetraacetylacetonate was recovered with 69% of the theoretical yield.

Zirconium Tri-n-propoxyacetylacetonate. Zirconium tetraacetylacetonate (5.15 g) was dissolved in excess n-propanol (30 ml). The acetylacetone evolved in the reaction was distilled off, in mixture with propanol, at 120-130°C. The evolution of acetylacetone ceased in 6 hours. On further heating of the reaction mixture with a fresh portion of propanol, no acetylacetone was detected in the receivers. The material in the reaction flask gave a positive test with $FeCl_3$. After thorough removal of traces of solvent at 1 mm and 75-80°C for one hour, there was obtained 3.78 g (97% of theoretical) of a viscous liquid, which was distilled at 10^{-4} mm. Found: C 45.89; 45.97; H 7.71; 7.90; Zr 25.08; 24.70%. $(n\text{-}C_3H_7O)_3ZrC_5H_7O_2$. Calculated: C 45.73; H 7.66; Zr 24.83%.

Action of Water on Iron Diacetylacetonate Chloride. Iron diacetylacetonate chloride [10] (2.15 g) was added to 4 ml of water, and the precipitate was filtered off and washed with water. The dried product did not contain chlorine. Yield 0.8 g, 45% of theoretical based on the equation:

$$3(C_5H_7O_2)_2FeCl + H_2O \rightarrow 2(C_5H_7O_2)_3Fe + FeCl_3$$

After recrystallization from a mixture of benzene and petroleum ether, the substance melted at 181-183°C. A mixed sample with iron triacetylacetonate did not give any melting-point depression.

Action of Water on Iron Dibenzoylacetonate Chloride. Iron dibenzoylacetonate chloride [10] (2 g) was added to water (10 ml) and allowed to stand for several days (poor wettability). The reaction mixture was filtered, and the residue was washed with water. The dried residue did not contain chlorine, and weighed 0.8 g (46% of theoretical). After recrystallization from benzene, the product melted at 217-218°C. Literature data [11]: m.p. 222-224°C. Found: C 66.59; 66.66; H 5.18; 5.12; Fe 10.29; 10.40%. $(C_{10}H_9O_2)_3Fe$. Calculated: C 66.79; H 5.04; Fe 10.36%.

Tetraacetoxytetraethoxytrititanoxane $(CH_3CO_2)_4(C_2H_5O)_4Ti_3O_2$. To a solution of 8.4 g (0.037 mole) of ethyl orthotitanate in 10 ml of dry benzene, a solution of 7.5 g (0.074 mole) of acetic anhydride in 5 ml of benzene was added dropwise. The ethyl acetate (to the extent formed) together with benzene was slowly distilled off with heating. The crystalline product remaining in the flask (7.5 g) was recrystallized twice from benzene. Found: C 32.62; 32.77; H 5.40; 5.49; Ti 23.92; 24.32; CH_3CO_2 39.67%. $(CH_3CO_2)_4(C_2H_5O)_4Ti_3O_2$. Calculated: C 32.43; H 5.40; Ti 24.32; CH_3CO_2 39.86%.

The molecular weight was determined by techniques permitting the application of the cryoscopic method for associated alkoxyl compounds of metals [12]. Found mol. wt. 592, 589. $(CH_3CO_2)_4(C_2H_5O)_4Ti_3O_2$. Calc. mol. wt. 591.

*[Refers to same footnote as that on English page 1490].

Substance	Found %			Calculated %		
	C	H	Zr	C	H	Zr
$(C_4H_9O)_6Zr_3O$ ($n=2$)	45,38 45,37	8,66 8,58	28,44 28,49	45,22	8,55	28,64
$(C_4H_9O)_8Zr_3O_2$ ($n=3$)	43,27 43,37	8,08 8,22	30,49 30,40	43,14	8,15	30,60
$(C_4H_9O)_{10}Zr_4O_3$ ($n=4$)	41,19 41,38	7,71 7,61	32,34 32,47	41,99	7,93	31,93
$(C_4H_9O)_{22}Zr_{10}O_9$ ($n=10$)	39,31 39,38	7,34 7,39	34,35 33,97	39,61	7,49	34,60

SUMMARY

1. A study has been made of the action of water on zirconium triacetylacetonate chloride, zirconium tribenzoylacetonate nitrate, zirconium isopropoxytriacetylacetonate, and the chlorides iron diacetyl- and dibenzoylacetonate. In all cases a disproportionation reaction took place, leading to the formation of zirconium tetraacetylacetonates or tetrabenzoylacetonates, or of iron triacetylacetonates or tribenzoylacetonates.

2. By the interaction of ethyl orthotitanate and acetic anhydride, taken in 1 : 2 mole ratio, there was obtained crystalline tetraacetoxytetraethoxytrititanoxane $(CH_3CO_2)_4(C_2H_5O)_4Ti_3O_2$.

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INTERACTION OF EPICHLOROHYDRIN WITH PHOSPHORUS ACID CHLORIDES

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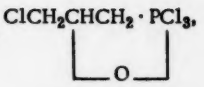
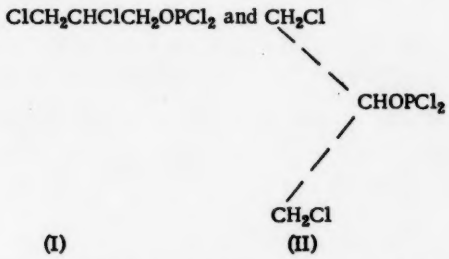
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1600-1606, September, 1961
Original article submitted February 20, 1961

In 1879 Hanriot [1] described the addition product of phosphorus trichloride and epichlorohydrin  , but the structure of the product was not established. Kabachnik and Rossiiskaya [2] in 1946 determined the structure of the addition products of phosphorus trichloride and ethylene oxide, and on this basis came to the conclusion that two possible formulas exist for the product of Hanriot:

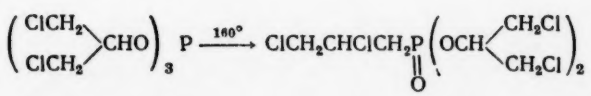


(I) (II)

By analogy with the addition product of epichlorohydrin and arsenic trichloride, the authors give preference to the second formula.

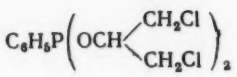
We have studied the interaction of epichlorohydrin with the chlorides of certain acids of phosphorus, namely: phosphorus trichloride, phenyldichlorophosphine, ethyldichlorophosphine, and methyldichlorophosphine oxide [dichloride of methylphosphonic acid]. Thereby the following results were obtained: The reaction between epichlorohydrin and phosphorus trichloride in equimolar ratio, in the presence of two or three drops of titanium tetrachloride, proceeds with considerable self-heating. Three fractions are obtained on distillation of the reaction products. Based on analytical data, and as we have established, the first fraction represents the dichloride of β,β'-dichloroisopropylphosphorous acid [β, β'-dichloroisopropoxydichlorophosphine]; it fumes strongly in air. The second fraction is the chloride of bis (β,β'-dichloroisopropyl) phosphorous acid [bis (β, β' -dichloroisopropoxy) chlorophosphine]. It also fumes in air, but more weakly. The third fraction is the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid. It will be shown below that the structures of these products actually correspond to the formulas named.

The interaction of epichlorohydrin with phosphorus trichloride in 3:1 mole ratio also proceeds with the evolution of heat. A thick yellow liquid is formed as a result of the reaction. During its vacuum distillation, the tris-(β,β'-dichloroisopropyl) phosphite formed in the reaction is isomerized into a derivative of pentavalent phosphorus, the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid, according to a mechanism proposed by Kabachnik and Rossiiskaya [3] for tri-β-chloroethyl phosphite:

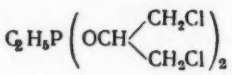


The isomerization occurs at a bath temperature ~ 160°C, and is accompanied by violent foaming of the material in the flask. The isomerization product is a transparent viscous liquid.

The reaction of epichlorohydrin with phenyldichlorophosphine and ethyldichlorophosphine in the presence of one or two drops of titanium tetrachloride proceeds with self-heating, especially strongly in the case of ethyldichlorophosphine. As a result of rearrangement of the reaction products, there are formed, respectively: 1) β,β'-dichloroisopropyl ester of β,γ-dichloropropylphenylphosphinic acid; 2) β,β'-dichloroisopropyl ester of β,γ-dichloropropylethylphosphinic acid. We had intended to isolate tris(β,β'-dichloroisopropyl) phosphite, the bis (β,β'-dichloroisopropyl) ester of phenylphosphonous acid:

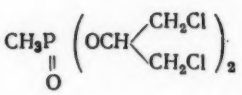


and the bis (β,β'-dichloroisopropyl) ester of ethylphosphonous acid:



by vacuum distillation at 0.02-0.05 mm; however, this was not successful, since the Arbuzov isomerization takes place at a bath temperature ~ 160°C for the first and second products and 150°C for the third product.

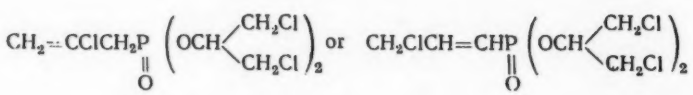
Epichlorohydrin enters into reaction with methyldichlorophosphine oxide[dichloride of methylphosphonic acid] on heating to 75-80°C. Subsequently the reaction proceeds with heat evolution, and only at the end is it again necessary to heat externally. The reaction product, the bis (β, β'-dichloroisopropyl) ester of methylphosphonic acid:



is a colorless, viscous liquid.

By the action of phosphorus pentachloride on the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid according to the methods of Kabachnik and Rossiiskaya[4] by the action of phosphorus pentachloride on the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid and on the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid in sealed tubes did not give the desired result.

The dehydrochlorination of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid by triethylamine in benzene solution by the method of Gefter [5] gave a colorless, viscous substance with b.p. 168-170°C (1 mm). The weight of the precipitated triethylamine hydrochloride that was formed during the dehydrohalogenation is evidence of the splitting of one HCl group. On this basis and from the analytical data, one of the following formulas can be ascribed to the product of dehydrochlorination:



In order to establish the structure of the products of interaction of epichlorohydrin with phosphorus acid chlorides, we performed a counter-synthesis: By the reaction between ethyldichlorophosphine and the α,γ-dichlorohydrin

of glycerin [1, 3-dichloroisopropanol], the bis (β,β'-dichloroisopropyl) ester of ethylphosphonous acid was obtained; this isomerized during vacuum distillation, and the β,β'-dichloroisopropyl ester of β,γ-dichloropropylethylphosphinic acid was isolated:

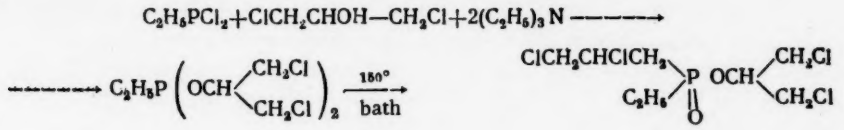
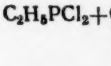
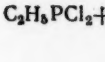


TABLE 1.

Method of preparation	B.p., °C (p, mm Hg)	n_D^{20}	P, %		Cl, %	
			Calc.	Found	Calc.	Found
$C_2H_5PCl_2$ + 	149—151 (0,05)	1,5055	9,8	9,57 9,96	44,88	44,61 44,47
$C_2H_5PCl_2$ + 	150—152 (0,05)	1,5057	9,8	9,62 9,91	44,88	44,69 44,58

A substance analogous in composition is formed, as was indicated previously, on the interaction of ethyldichlorophosphine with epichlorohydrin (direct synthesis).

A comparison of the physicochemical constants of the products of the direct and counter syntheses indicates that they are fully identical (Table 1). The infrared absorption spectra of the compounds compared also proved to be completely identical (Figs. 1 and 2). These data allow drawing the conclusion that the products of interaction of epichlorohydrin with phosphorus acid chlorides have an iso-structure. The physicochemical constants and analyses of the substances that we obtained are shown in Table 2.

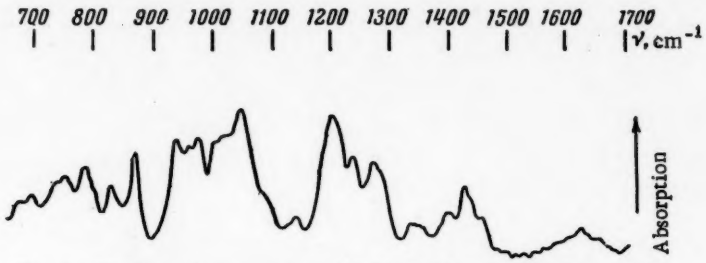


Fig. 1. IR absorption spectrum of β,β'-dichloroisopropyl ester of β, γ-dichloropropylethylphosphinic acid from direct synthesis.

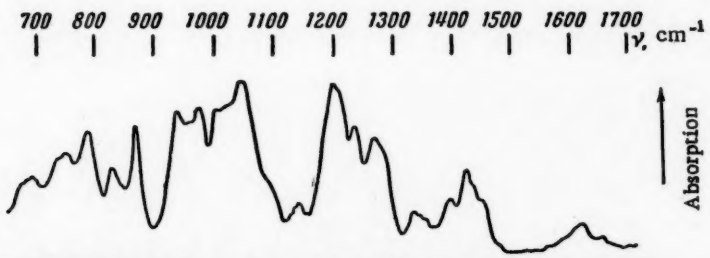


Fig. 2. IR absorption spectrum of β,β'-dichloroisopropyl ester of β, γ-dichloropropylethylphosphinic acid from counter synthesis.

TABLE 2.

Formula	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR Found	MR Calc.	P, % Found	P, % Calc	Cl, % Found	Cl, % Calc.	Yield, %
$ClCH_2CH(ClCH_2)CHOPCl_2$*	49—51 (1)	1,5222	1,5296	45,83	45,37	13,75 13,39	13,47	61,27 61,20	61,69	28
$[ClCH_2CH(ClCH_2)CHO]_2PCl$**	122—124 (1)	1,5183	1,4605	65,58	65,72	9,19 9,31	9,6	55,4 55,01	54,98	26
$ClCH_2CHClCH_2P(=O)[OCH(CH_2Cl)CH_2Cl]_2$***	170—172 (0,02)	1,5148	1,4823	84,38	83,39	7,28 7,03	7,46	51,12 51,38	51,27	47,5
$ClCH_2CHClCH_2C_6H_4P(=O)OCH(CH_2Cl)CH_2Cl$	179—181 (0,02)	1,5528	—	—	—	8,8 9,0	8,51	39,13 39,25	38,95	88
$CH_3P(=O)[OCH(CH_2Cl)CH_2Cl]_2$	127—129 (1)	1,4922	1,4391	64,43	64,86	9,25 9,38	9,75	44,56 44,8	44,6	75
$ClCH_2CHClCH_2C_6H_4P(=O)OCH(CH_2Cl)CH_2Cl$	149—151 (0,05)	1,5055	1,3768	68,14	68,34	9,57 9,96	9,8	44,61 44,47	44,88	54
$ClCH_2CH{=}CHP(=O)[OCH(CH_2Cl)CH_2Cl]_2$****	168—170 (1)	1,5102	—	—	—	7,83 7,68	8,18	46,55 46,83	46,84	47
$ClCH_2CHClCH_2P(=O)(Cl)OCH(CH_2Cl)CH_2Cl$	188—190 (8)	1,5168	—	—	—	9,27 9,42	9,6	55,44 55,8	54,98	43

* B. p., 75° (2 mm); d_4^{20} 1.4973; n_D^{20} 1.5195 [6].

** B. p. 135—137° (1 mm); d_4^{20} 1.4903; n_D^{20} 1.5189 [6].

*** B. p. 208—210° (2 mm); d_4^{20} 1.5018; n_D^{20} 1.5130 [6].

**** The other possible formula of this substance is $CH_2=CClCH_2P(=O)[OCH(CH_2Cl)CH_2Cl]_2$

EXPERIMENTAL

Synthesis of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylethylphosphinic Acid. In a four-necked flask with mechanical stirrer, reflux condenser, dropping funnel, thermometer, and CO_2 inlet tube, 20 g (0.21 mole) of epichlorohydrin was placed, and 2 drops of $TiCl_4$ was added. In a stream of CO_2, 13.1 g (0.1 mole) of ethyldichlorophosphine was added dropwise. Since the reaction takes place with heat evolution, the flask was cooled periodically in a water bath. The rate of dropping and the cooling were regulated to maintain the temperature in the flask at 50-55°C. At the end of the reaction, the mixture was stirred at room temperature for 4 hours. The product was vacuum distilled from an Arbuzov flask. At a bath temperature ~ 150°C isomerization was observed, accompanied by violent foaming of the material in the flask. Recovered 17 g (54% theor.) of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylethylphosphinic acid, with b.p. 149-151°C (0.05 mm); n_D^{20} 1.5055; d_4^{20} 1.3768. Found: P 9.57; 9.96; Cl 44.61; 44.47%: MR 68.13. $C_8H_{15}O_2PCl_4$. Calculated: P 9.8; Cl 44.88%; MR 68.34;

In the subsequent descriptions, all reactions between epichlorohydrin and phosphorus acid chlorides were carried out in the apparatus described above.

Synthesis of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylethylphosphinic Acid. [Counter-Synthesis] Synthesis of the ester by interaction of ethyldichlorophosphine with the α,γ-dichlorohydrin of glycerin [1,3-dichloroisopropanol] was carried out in the apparatus described above. The flask was charged with 13.1 g of ethyldichlorophosphine and 200 ml of dry ether. By means of the dropping funnel, in a CO_2 stream there was added a solution of 25.8 g of α,γ-dichlorohydrin of glycerin and 20.3 g of triethylamine in 100 ml of dry ether. The reaction mixture was cooled with snow–salt mixture. Stirring of the reaction products was continued 2 hours at room temperature. The precipitated triethylamine hydrochloride was filtered off, and the residue after removing the ether was vacuum distilled from an Arbuzov flask. At a bath temperature ~ 150°C, rearrangement took place (violent foaming of liquid). Recovered 15.4 g (49%) of a substance with b.p. 150–152° (0.05 mm); n_D^{20} 1.5057; d_4^{20} 1.3763. Found: P 9.62; 9.91; Cl 44.58; 44.69% MR 68.29. $C_8H_{15}O_2PCl_4$. Calculated: P 9.8; Cl 44.88%; MR 68.34.

Synthesis of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylphenylphosphinic Acid. Phenyldichlorophosphine 19 g and epichlorohydrin 21 g were taken for reaction. The product was vacuum distilled from an Arbuzov flask. During distillation, isomerization took place at a bath temperature ~ 160°C. Obtained 35 g (88% theor.) of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphenylphosphinic acid, with b. p. 179–181° (0.02 mm); n_D^{20} 1.5528. Found: P 8.8; 9.0; Cl 39.13; 39.25; C 40.4; 40.2; H 4.3; 4.2%. $C_{12}H_{15}O_2PCl_4$. Calculated: P 8.51; Cl 38.96; C 39.58; H 4.16%.

Interaction of Epichlorohydrin with Phosphorus Trichloride in 1:1 Ratio. Phosphorus trichloride 20 g and epichlorohydrin 13.5 g were taken for reaction. The reaction products were vacuum distilled from an Arbuzov flask. Obtained: 1) Dichloride of β,β'-dichloroisopropylphosphorous acid [β,β'-dichloroisopropoxydichlorophosphine], with b.p. 49-51° (1 mm); 9.5 g (28% theor.); n_D^{20} 1.5222; d_4^{20} 1.5296. Found: P 13.75; 13.39; Cl 61.27; 61.20%; MR 45.83. $C_3H_5OPCl_4$. Calculated: P 13.47; Cl 61.69%; MR 45.37. 2) chloride of bis (β,β'-dichloroisopropylphosphorous acid [bis (β,β'-dichloroisopropoxy) chlorophosphine], with b.p. 122-124° (1 mm); 12.2 g (26% theor.) n_D^{20} 1.5183; d_4^{20} 1.4905. Found: P 9.19; 9.60; Cl 55.01; 55.4%; MR 65.58. $C_6H_{10}O_2PCl_5$. Calculated: P 9.6; Cl 54.98%; MR 65.72. 3) bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid, with b.p. 170-172° (0.02 mm); 2.8 g (4.7% theor.); n_D^{20} 1.5148; d_4^{20} 1.4823. Found: P 7.28; 7.95; Cl 51.12; 51.38%; MR 84.38. $C_9H_{15}O_3PCl_6$. Calculated: P 7.46; Cl 51.27%; MR 83.89.

Interaction of Phosphorus Trichloride with Epichlorohydrin in 1:3 Ratio. Epichlorohydrin 70 g and phosphorus trichloride 35 g were taken for the synthesis. The reaction was conducted at 35-40°C. During distillation of the reaction products, isomerization occurred at a bath temperature ~ 160°C. Obtained 50 g (47.5 % theor.) of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid, with b.p. 170–172° (0.02 mm): n_D^{20} 1.5147; d_4^{20} 1.4820.

Synthesis of Chloride of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylphosphonic Acid. In a four-necked round-bottom flask with mechanical stirrer, reflux condenser, and thermometer, 20 g of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid was heated to 140°C. At this temperature, 20.5 g of phosphorus pentachloride was introduced in small portions. Then the reaction mixture was stirred 6 hours at a bath temperature of 150-155°C. The phosphorus oxychloride was distilled off, and the residue was vacuum fractionated from an Arbuzov flask in a stream of dry CO_2. After two distillations, there was obtained 6.5 g (43% theor.) of the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid, with b.p. 188–190°C. (8 mm); n_D^{20} 1.5168. Found: P 9.27; 9.42; Cl 55.44; 55.80%. $C_6H_{10}O_2PCl_5$. Calculated: P 9.6; Cl 54.98%.

Interaction of Bis (β,β'-Dichloroisopropyl) Ester of β,γ-Dichloropropylphosphonic Acid with Phosphorus Pentachloride, under Pressure. A mixture of 12.7 g of the bis (β,β'-dichloroisopropoyl) ester of β,γ-dichloropropylphosphonic acid and 13 g of phosphorus pentachloride was heated in a sealed tube at 145-150°C for 2 hours. After cooling, the contents of the tube was vacuum distilled. Obtained two fractions: 1) 30-68°C (8 mm) 6.7 g; 2) 185-188°C (8 mm) 7.2 g. On redistillation of the second fraction, obtained 5.4 g of a substance with b.p. 188-190°C (8 mm); n_D^{20} 1.5166. Found: P 9.19; 9.31; Cl 55.38; 55.72%. Based on the constants and the elemental analysis, the product obtained was the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid; yield 55% of theoretical.

Interaction of Chloride of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylphosphonic Acid with Phosphorus Pentachloride, under Pressure. A mixture of 6.5 g of the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid and 4.5 g of phosphorus pentachloride was heated in a sealed tube for 8 hours at 165-170°c. The resulting transparent liquid was distilled from an Arbuzov flask. The reaction products were not successfully identified.

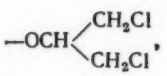
Dehydrochlorination of Bis (β,β'-Dichloroisopropyl) Ester of β,γ-Dichloropropylphosphonic Acid. A three-necked flask, fitted with a mechanical stirrer, reflux condenser, and thermometer, was charged with 18.5 g of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid, 9 g of triethylamine, and 40 ml of dry benzene. The reaction mixture was stirred with heating 3 hours at 30°C, 2 hours at 60°C, and 3 hours at 80°C, and was allowed to stand overnight. After filtering off the precipitate and removing the solvent by evaporating under vacuum, the filtrate was vacuum distilled from an Arbuzov flask. Recovered 2.8 g (47% theor.) of a substance with b.p. 168-170°C (1 mm); n_D^{20} 1.5102. Found: P 7.83; 7.68; Cl 46.55; 46.83%. Based on the elemental analysis, the substance corresponds to the formula $C_9H_{14}O_3PCl_3$, for which the calculated values are P 8.8, Cl 46.84%.

The authors express thanks to R. Shagidullin for taking the infrared absorption spectra of a number of the substances.

SUMMARY

1. Phosphorus acid chlorides react with epichlorohydrin according to the scheme proposed by Kabachnik and Rossiiskaya for the interaction of phosphorus trichloride with ethylene oxide.

2. It was established by a counter-synthesis method and by spectrum analysis that in the products of the addition of epichlorohydrin to phosphorus acid chlorides the ester groups have the iso-structure:



and not the linear structure $-OCH_2CHClCH_2Cl$.

3. At a bath temperature ~160°, tris (β,β'-dichloroisopropyl) phosphite undergoes the Arbuzov rearrangement, with the formation of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid.

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FLUORINE CONTAINING β-SULTONES

PART 11. PREPARATION OF FLUOROMETHANESULFONYL FLUORIDE AND DIFLUOROMETHANESULFONYL FLUORIDE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1606-1610, September, 1961
Original article submitted January 2, 1961

In previous reports it has been shown [1,2] that the corresponding fluorine substituted fluorosulfonylcarboxylic acids are formed when fluorine containing β-sultones are hydrolysed. In this way it was noted that fluorosulfonylmonofluoroacetic and fluorosulfonyldiacetic acids were comparatively stable compounds. However, it was noted at the same time that when these acids were heated for many hours at 160-180°C they were observed to decompose with the evolution of gaseous products, among which was carbon dioxide. If the acids were moistened their decomposition was observed at much lower temperatures; in certain cases it even occurred spontaneously in glass. In this connection it appeared interesting to investigate the decarboxylation of fluorosulfonylmonofluoroacetic and fluorosulfonyldifluoroacetic acids, which might lead in part to the formation of fluorinated methanesulfonyl fluorides. The present communication is concerned with the study of this problem.

It is known that the decarboxylation of carboxylic acids is in general easily accomplished by heating the dry alkali metal salt or by heating an aqueous solution of the acid. It was shown that, when a 20% aqueous solution of fluorosulfonyldifluoroacetic acid was heated at up to 40-50°C, evolution of gaseous products was observed, and this became especially vigorous at 80-90°C. Among the reaction products carbon monoxide, carbon dioxide, sulfur dioxide, and difluoromethanesulfonyl fluoride (condensed as a liquid) were detected; hydrofluoric, oxalic and sulfonyldifluoroacetic acids were detected in the aqueous solution. The formation of the substances enumerated may be explained by the simultaneous occurrence of several concurrent processes:

$$F-SO_2-CF_2-COOH \xrightarrow{+H_2O} F-SO_2-CF_2H + CO_2 \quad (1)$$

$$F-SO_2-CF_2-COOH \xrightarrow{+H_2O} HO-SO_2-CF_2-COOH + HF \quad (2)$$

$$F-SO_2-CF_2-COOH \xrightarrow{+H_2O} [F-SO_2-H + HO-CF_2-COOH] \xrightarrow{+H_2O} SO_2 + CO + CO_2 + H_2O \quad (3)$$

$$+ 3HF + (COOH)_2$$

With a decreased concentration of fluorosulfonyldifluoroacetic acid and a decreased contact time with water it is possible to increase the yield from the decarboxylation process. Thus when a 20-30% aqueous solution of the acid was slowly heated to 100°C the yield of difluoromethanesulfonyl fluoride did not exceed 18%. If the acid was gradually dropped into boiling water then the conversions of the acid according to the reactions (1)-(3) were 25,30, and 45% respectively.

The explanation of the role of the factors under discussion is in agreement with general ideas on the mechanism of decarboxylation:

$$F-SO_2-CF_2-COOH \rightleftharpoons F-SO_2-CF_2-COO^- + H^+ \quad (a)$$

$$F-SO_2-CF_2-COO^- \rightarrow F-SO_2-CF_2^- + CO_2 \quad (b)$$

$$F-SO_2-CF_2^- + H^+ \rightarrow F-SO_2-CF_2H \quad (c)$$

The decreased concentration of fluorosulfonyldifluoroacetic acid facilitates dissociation of the acid with formation of the carboxyanion (a) and hinders hydrolysis (2). An increase in temperature facilitates the decomposition of the carboxyanion into the carbanion (b) and also facilitates reaction (3) in its first stage. The simultaneous occurrence and similar rate of processes (b) and (3) is explained by the negligible difference between the bond energies C–C and S–C. It is interesting to note that the decomposition of sulfonylacetic acid is also described by two concurrent processes: decarboxylation and elimination of sulfur trioxide (3). Heating a solution of fluorosulfonyldifluoroacetic acid in aqueous glycerol is also accompanied by decomposition of the acid with the formation of difluoromethanesulfonyl fluoride; the yield however does not exceed 20%.

Fluoromethanesulfonyl fluoride was obtained by a similar decomposition of fluorosulfonylmonofluoroacetic acid. When the reaction was carried out by dropping the acid into boiling water the yield of fluoromethanesulfonyl fluoride was 20%, and on heating an aqueous glycerol solution of the acid it was 18%. Fluoromethane and difluoromethanesulfonyl fluoride are colorless heavy volatile liquids with weak unpleasant smells; they do not dissolve in water but they are soluble in most organic solvents. Some constants of the compounds obtained are cited in Table 1 (methane–and trifluoromethane- sulfonyl fluoride are included in Table 1 for comparison).

TABLE 1.

Formula	B. p. °C	d_4^{20}	n_D^{20}	MR*	
				Found	Calculated
CH_3-SO_2-F	123	–	–	–	–
CH_2F-SO_2-F	101	1.5515	1.3479	15.965	16.185
CHF_2-SO_2-F	52	1.5789	1.3100	16.365	16.154
CF_3-SO_2-F	–22	–	–	–	–

* The molecular refractions of fluoromethane- and difluoromethane- sulfonyl fluoride were calculated using the value for the group refractivity of the fluorosulfonyl group R_{SO_2F} = 10.541 [5].

TABLE 2.

Formula	Yield %	B. p. °C (p, mm Hg)	d_4^{20}	n_D^{20}
$CH_3-SO_2-N(C_2H_5)_2$	96	105 (6)	1.1953	1.4452
$CH_2F-SO_2-N(C_2H_5)_2$	81	65 (03)	1.199	1.4370
$CHF_2-SO_2-N(C_2H_5)_2$	20	55 (3)	1.2214	1.4030

It is interesting to note that in distinction from the trifluoromethanesulfonyl fluoride the partially fluorinated analogues are comparatively reactive substances. Thus difluoromethanesulfonyl fluoride is hydrolyzed even by standing for several days over water. The degree of mobility of the acid fluoride fluorine may be characterized by its reaction with amines. For example, methanesulfonyl fluoride reacts with diethylamine without noticeable signs of reaction whereas the analogous reaction with fluoromethanesulfonyl fluoride occurs with noticeable heating of the mixture; the reaction with difluoromethanesulfonyl fluoride is characterized by extremely energetic reaction. In all three cases the products of the reactions are the corresponding sulfonamides, some physical constants of which are cited in Table 2.

EXPERIMENTAL

Decarboxylation of Fluorosulfonyldifluoroacetic Acid. 19.9 g of freshly prepared fluorosulfonyldifluoroacetic acid was added to 200 ml boiling water; the reaction mixture was observed to boil vigorously where the drops fell, and liquid and gaseous products were evolved. The liquid products were collected in a trap cooled to 0°C and the gaseous products were condensed in a trap cooled to -78°C. The non-condensed gases were collected in a gasometer over water. The distillate (3.6 g) was washed with iced water, dried over magnesium sulfate, and redistilled, in this way a colorless mobile liquid, which was shown to be difluoromethanesulfonyl fluoride, was collected. Found: C 8.93;

H 1.06; F 42.85%; mol. wt. 133.2; and equal 2.05. CHO_2F_3S. Calculated: C 8.95; H 0.75; F 42.55%; mol.wt. 134.1; and equal 2.00.

The condensate collected in the tube (3.2 g) was shown to be sulfur dioxide with b.p. -10 to -9°C. Found: mol. wt. 63.0 iodine eqv 1.95; yield 45.3%. The gaseous reaction products consisted of carbon dioxide (tested with aqueous barium hydroxide) and carbon monoxide (tested with palladium chloride). On passing the gas mixture through a tube containing soda lime the increase in known weight was 3.5 g which corresponds to 70.5% carbon dioxide. The reaction mixture was an aqueous solution containing fluoride ions (59.5%) and oxalate ions. Evaporation of the solution, neutralized with sodium hydroxide, and multiple crystallization of the dry residue gave sodium hydrogen fluoride and disodium sulfonyldifluoroacetate. Found: F 16.90; S 14.32%. $C_2O_5F_2SNa_2$. Calculated: F 17.20; S 14.57%.

When the reaction was carried out by heating a solution of 14 g of fluorosulfonyldifluoroacetic acid in 60 ml water 1.9 g difluoromethanesulfonyl fluoride (17%) was separated together with 1.2 g sulfur dioxide (35%) and 1.45 g carbon dioxide (26.5%). On heating a solution of 15 g fluorosulfonyldifluoroacetic acid in a mixture of 30 ml water and 30 ml glycerol at 90-100°C 1.9 g difluoromethanesulfonyl fluoride (19.5%), 1.7 g carbon dioxide (47%) and 2.0 g sulfur dioxide (37%) separated.

Decarboxylation of Fluorosulfonylmonofluoroacetic Acid. A solution of 15.5 g of fluorosulfonylmonofluoroacetic acid in 60 ml water was heated until a liquid fraction began to boil off (~ 60-70°C), and it was slowly distilled until the gaseous reaction products had completely separated. In this way a distillate was collected which separated into two layers in the trap. The lower layer was separated, washed with iced water, dried over magnesium sulfate, and distilled. 2.2 g fluoromethanesulfonyl fluoride separated. Found: C 10.69; H 1.87; F 33.39; S 27.82%; mol. wt. 115.1; and equals 1.98. $CH_2O_2F_2S$ Calculated: C 10.34; H 1.72; F 33.75; S 27.58%; mol. wt. 116.2; and equals 2.00. Yield 20%.

When the reaction was carried out by heating a solution of 9.9 g of fluorosulfonylmonofluoroacetic acid in a mixture of 25 ml water and 25 ml glycerol at 100°C, 1.8 g fluoromethanesulfonyl fluoride (18%) separated.

Preparation of N, N-diethylmethanesulfonamide. A mixture of 10 g diethylamine and 4.5 g methanesulfonyl fluoride was kept for a day at room temperature, and the semiliquid mass was decomposed with 20 ml water. The lower layer was separated, washed with water, and added to the ether extracts of the upper layer. The ethereal solution was dried over magnesium sulfate and fractionated. 6.7 g of N, N-diethylmethanesulfonamide was obtained. Found: N 9.17%. $C_5H_{13}O_2NS$. Calculated: N 9.27%. Yield 96.5%.

Preparation of N, N-diethylfluoromethanesulfonamide. In a similar manner 1.6 g of N, N-diethylfluoromethanesulfonamide was obtained from 1.3 g fluoromethanesulfonyl fluoride and 2.6 g diethylamine. Found: C 35.55; H 7.13; N 8.05%. $C_5H_{12}O_2$ NFS. Calculated: C 35.50; H 7.10; N 8.28%. Yield 81%.

Preparation of N, N-diethyldifluoromethanesulfonamide. A solution of 5.2 g diethylamine in 20 ml dry ether was added cautiously to 2.7 g difluoromethanesulfonyl fluoride which was maintained at 10°C. The reaction mass was washed with 10 ml water. The ethereal solution was dried over magnesium sulfate and fractionated. 0.7 g of N, N-diethyldifluoromethanesulfonamide was separated. Found: N 7.22 F 20.95%. $C_5H_{11}O_2NF_2S$. Calculated: N 7.48; F 20.32%. Yield 20%.

SUMMARY

1. The decomposition of fluorosulfonylmonofluoroacetic and fluorosulfonyldifluoroacetic acids in aqueous solution has been studied.

2. Fluoromethane- and difluoromethane-sulfonyl fluoride have been prepared and some of their properities studied.

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ON THE TELOMERIZATION REACTION OF DIMETHYLCYCLOSILOXANES

ARTICLE 2. PREPARATION OF LINEAR α-CHLORO-ω-TRIMETHYLSILOXYDIMETHYLSILOXANES

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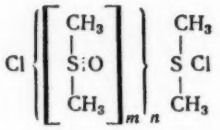
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9,
pp. 1610-1615, September, 1961
Original article submitted November 28, 1960

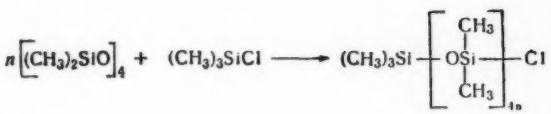
A method for preparing oligomeric dimethylsiloxanes with a functional group at one end of the siloxane chain, is described in the literature [1]. The authors proceed from oligomeric α, ω-dichlorodimethylsiloxanes prepared by the partial hydrolysis of dimethyldichlorosilane. By replacing one of the end chlorine atoms with an organic radical by means of organolithium compounds, linear dimethylsiloxanes, having one to five silicon atoms in the molecule, with a chlorine atom at one end of the siloxane chain, can be obtained in yields up to 40%. In the preceding articles [2,3] we showed that the reaction of dimethyldichlorosilane with dimethylcyclosiloxanes gives a series of α, ω-dichlorodimethylsiloxanes having the following structure:



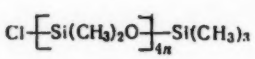
where m is the number of silicon atoms in the original ring, and n= 1,2,3, etc.

It was of interest to carry out the telomerization reaction of dimethylcyclosiloxanes, using not a difunctional compound but a monofunctional one as the chain-terminating substance.

The present article is devoted to a description of the reaction of octamethylcyclotetrasiloxane with trimethylchlorosilane. When the reaction is carried out between equimolar quantities of the indicated substances at a temperature of 250°C for 5 hr, it goes according to the equation:

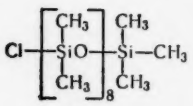
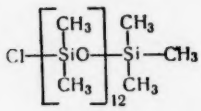
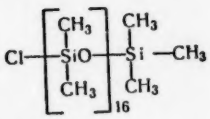


As in the case of the interaction of dimethyldichlorosilane and octamethylcyclotetrasiloxanes, the mechanism of the given reaction apparently consists in coordination of the trimethylchlorosilane silicon atom with an octamethylcyclotetrasiloxane oxygen atom, followed by ring rupture. In this case the chlorine atom combines with the octamethylcyclotetrasiloxane silicon atom, and the trimethylsilyl group goes to the oxygen atom. Further chain growth also takes place through the coordination of the terminal silicon atom, bound to halogen, and the octamethylcyclotetrasiloxane oxygen atom. Subsequent ring cleavage and formation of a new siloxane bond leads to lengthening of the chain by four dimethylsiloxane links. Thus members of a homologous series of the following composition are obtained:



Telomers with n = 2, 3, and 4 were isolated from the reaction mixture. The properties of these products are given in Table 1.

TABLE 1. Physical Properties of α-Chloro-ω-trimethylsiloxydimethylsiloxanes

Formula	Physical Properties				
	b.p., °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR found	MR calc.
	197—199 (20)	0,9535	1,4012	178,84	179,03
	194—196 (3)	0,9592	1,4023	253,52	253,89
	233—235 (3)	0,9655	1,4035	327,52	328,50

The first member of the series (n = 1) was not isolated in pure form owing to the relative proximity of the boiling points of octamethylcyclotetrasiloxane and 1-chlorohendecamethylpentasiloxane, as a result of which the chlorine content in the fraction with b.p. 123-127°C (20 mm), corresponding to this monochloride [1], was invariably diminished appreciably.

In order to prove the presence of 1-chlorohendecamethylpentasiloxane the corresponding fraction was hydrolyzed and then condensed to the dimer—diicosamethyldecasiloxane—which was then identified by the boiling point, specific gravity, refractive index, molar refraction, and data of elementary analysis (Table 2). Investigation of the physical properties of members of the homologous series of Formula 1 with respect to the number of silicon atoms in the molecule revealed no anomalies in the properties of the telomeric homologs. The boiling points, specific gravities, and refractive indices vary regularly as the number of silicon atoms is increased.

When the effect of the molar ratio of octamethylcyclotetrasiloxane to trimethylchlorosilane in the original mixture on the composition of the reaction products was studied, it was found that the telomerization reaction does not lead to the formation of any one individual compound at any of the ratios investigated (1 : 1, 2 : 1, 3 : 1); a mixture of telomers is always formed. In this case the maximum yield is observed for a telomer with a chain length greater by four dimethylsiloxane links than that corresponding to the stoichiometric ratio in the original mixture. Thus when the ratio of octamethylcyclotetrasiloxane to trimethylchlorosilane is 1 : 1, not monochloropentasiloxane but monochlorononasiloxane is obtained in maximum yield, etc.

Curves of distribution according to molecular weight for different ratios of reacting components are shown in Fig. 1. In Fig. 2 the yields of various reaction products are shown with respect to the initial ratio of octamethylcyclotetrasiloxane to trimethylchlorosilane; from these it is evident that an increase in the given ratio leads to a decrease in the yield of lower telomers and a sharp increase in the yield of high-boiling products. It is also evident that a decrease in the content of trimethylchlorosilane, which opens up the octamethylcyclotetrasiloxane, in the original mixture in the region of the ratios studied, does not diminish the degree of conversion of octamethylcyclotetrasiloxane.

EXPERIMENTAL

Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane. Octamethylcyclotetrasiloxane (b.p. 174-176°C, mol. wt. 296.5) and trimethylchlorosilane (b.p. 57-57.5°C, mol. wt. 108.6; Cl 32.8%) were used for the syntheses. Into a dry, stainless steel autoclave of 0.5-liter capacity was put a mixture of the calculated quantities

of octamethylcyclotetrasiloxane and trimethylchlorosilane. The apparatus was kept at 250°C for 5 hr, cooled, and the reaction mixture fractionated. The fractionation was done by means of Favorskii flask with a 25 mm fractionating column. The percentage of chlorine was determined by titration in all fractions collected. Data on the charge in the apparatus, material balance of fractionation, and determination of the percentage of chlorine in the fractions, and also the results of calculation of the content of pure products in the intermediate fractions, are given for studied ratios of octamethylcyclotetrasiloxane to trimethylchlorosilane, equal to 1 : 1, 2 : 1, and 3 : 1 in Tables 3, 4, and 5, respectively. Fractions IV, VI, and VII (Table 3) were distilled twice, the following pure products being isolated: $Cl[(CH_3)_2SiO]_8Si(CH_3)_3$, $Cl[(CH_3)_2SiO]_{12}Si(CH_3)_3$ and $Cl[(CH_3)_2SiO]_{16}Si(CH_3)_3$, analytical data for which are given in Table 6.

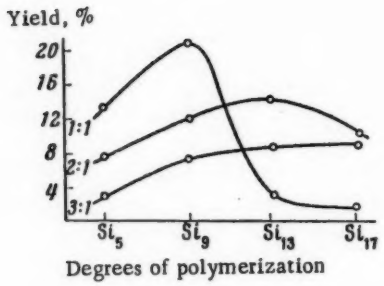


Fig. 1

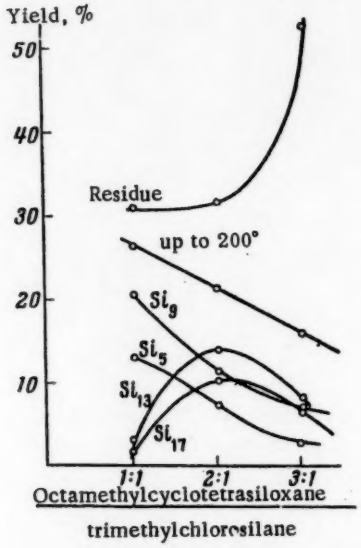


Fig. 2

TABLE 2. Physical Properties of Diicosamethyldecasiloxane

Data	Physical properties				Analytical data, %		
	B.p., °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR	C	H	Si
Experimental	168—170 (2)	0,9254	1,3982	197,08	35,29 35,19	8,61 8,62	37,38 37,25
Literature and calculated	176 (3) 161 (1,1)	0,925	1,3988	198,46	34,98	8,81	37,15

Preparation of Diicosamethyldecasiloxane. A 25.8 g quantity of the product (fraction II, Table 4) with a chlorine content of 4.15; 4.10% was stirred with 30 g of water at 20°. The upper, oil layer was separated and was condensed by refluxing at 120°C for 3 hr. Then it was washed with water to remove HCl, dried, and distilled in vacuo. There was obtained 7.28 g of a fraction boiling at 165-173°C (2 mm) (63%). On distillation of this fraction pure diicosamethyldecasiloxane, $(CH_3)_3SiO[Si(CH_3)_2O]Si(CH_3)_3$ Found: C 35.29; 35.19; H 8.61; 8.62; Si 37.38; 37.25%. Calculated: C 34.98; H 8.81; Si 37.15%. The physical properties of this compound are given in Table 2.

SUMMARY

1. The telomerization reaction of octamethylcyclotetrasiloxane with trimethylchlorosilane leads to the formation of telomeric homologs of linear structure, having the composition: $Cl[(CH_3)_2SiO]_{4n}-Si(CH_3)_3$.

TABLE 3.* Results of the Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane at the Ratio 1:1. [The autoclave was charged with 293 g of a mixture containing 214.5 g (0.724 mole) of octamethylcyclotetrasiloxane and 78.5 g (0.724 mole) of trimethylchlorosilane. After the reaction 288 g was recovered; 280 g was subjected to fractionation.]

Fraction	B.p., °C (p, mm Hg)	Yield, g	Cl content, %	Content in fractions, g			
				Si_5 calculated Cl=8.75%	Si_9 calc. Cl=5.05%	Si_{13} calc. Cl=3.55%	Si_{17} calc. Cl=2.74%
I	up to 200 (760)	67,00	— —	—	—	—	—
II	up to 100 (20)	5,72	6,63; 6,81	4,41	—	—	—
III	100—130 (20)	24,81	6,50; 6,55	18,50	—	—	—
IV	130—185 (20)	29,45	6,10; 6,57	10,15	19,30	—	—
V	185—225 (20)	27,63	5,33; 5,38	2,28	25,35	—	—
VI	195 (3)	16,74	6,04; 5,62	2,62	14,12	—	—
VII	195—220 (3)	8,57	3,67; 3,25	—	—	8,57	—
VIII	220—240 (3)	6,32	2,28; 2,40	—	—	—	5,40
IX	240—280 (3)	17,46	1,57; 1,70	—	—	—	—
X	Residue (3)	70,34	— —	—	—	—	—
	Losses —	5,96	— —	—	—	—	—
Total g		280	—	37,96	58,77	8,57	5,40
%		100	—	13,56	20,99	3,06	1,93

* In Tables 3 - 5 the yield of telomers was calculated with allowance for their content in the intermediate stages.

TABLE 4.* Results of the Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane at the Ratio 2:1. [The autoclave was charged with 307.6 g of a mixture containing 260 g (0.876 mole) of octamethylcyclotetrasiloxane and 47.6 g (0.438 mole) of trimethylchlorosilane. After the reaction 303.16 g was recovered; 299 g was subjected to fractionation.]

Fraction	B.p., °C (p, mm Hg)	Yield, g	Cl Content found, %	Content in fractions, g			
				Si_5 calc. Cl=8.75%	Si_9 calc. Cl=5.05%	Si_{13} calc. Cl=3.55%	Si_{17} calc. Cl=2.74%
I	up to 195 (760)	47,70	— —	—	—	—	—
II	up to 130 (20)	25,84	4,15; 4,10	12,16	—	—	—
III	135—150 (20)	11,25	5,72; 5,47	7,20	—	—	—
IV	150—200 (20)	27,60	5,35; 5,67	3,40	24,20	—	—
V	200—230 (20)	21,66	4,56; 4,15	—	11,55	10,11	—
VI	190—210 (3)	19,09	3,49; 3,59	—	—	19,09	—
VII	210—230 (3)	21,81	3,24; 3,26	—	—	13,74	8,07
VIII	230—250 (3)	24,02	2,75; 2,56	—	—	—	24,02
IX	250—280 (3)	29,50	1,09; 0,98	—	—	—	—
X	Residue (3)	66,23	— —	—	—	—	—
	Losses	4,30	— —	—	—	—	—
Total g		299	— —	22,76	35,75	42,94	32,09
%		100	— —	7,61	11,96	14,36	10,73

* See footnote - Table 3.

2. New compounds—telomeric homologs containing one chlorine and nine, thirteen, and seventeen silicon atoms in the molecule—were identified and their physical properties studied.

3. The maximum yield of telomers does not correspond to the stoichiometric ratio (n) of the reacting components, but is shifted by one order (n+1) toward the formation of telomers of higher molecular weight.

TABLE 5.* Results of the Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane at the Ratio 3:1. [The autoclave was charged with 203.8 g of a mixture containing 181.7 g (0.612 mole) of octamethylcyclotetrasiloxane and 22.1 g (0.204 mole) of trimethylchlorosilane. After the reaction 199.50 g was recovered; 186.8 g was subjected to fractionation.]

Fraction	B.p., °C (p, mm Hg)	Yield, g	Cl content found, %	Content in fractions, g			
				Si_5 calc. Cl=8.75%	Si_9 calc. Cl=5.05%	Si_{13} calc. Cl=3.59%	Si_{17} calc. Cl=2.74%
I	up to 195 (760)	20,68	— —	—	—	—	—
II	up to 130 (20)	11,88	3,02; 2,80	3,96	—	—	—
III	130- 150 (20)	3,80	4,05; 4,12	1,78	—	—	—
IV	150—200 (20)	8,35	4,75; 4,69	—	6,51	1,84	—
V	200—230 (20)	9,0	4,23; 4,13	—	3,78	5,22	—
VI	To 190 (3)	8,10	3,93; 4,11	—	2,54	5,56	—
VII	190—225 (3)	10,27	2,99; 3,00	—	—	3,29	6,98
VIII	225—250 (3)	10,17	2,41; 2,46	—	—	—	10,17
IX	250—280 (3)	8,86	0,62; 1,10	—	—	—	—
X	Residue (3)	91,6	— —	—	—	—	—
	Losses	4,09	— —	—	—	—	—
Total	g	186,8	— —	5,74	12,83	15,91	17,15
	%	100	— —	3,07	7,40	8,52	9,18

* See footnote - Table 3.

TABLE 6. $Cl[(CH_3)_3SiO]_{4n}Si(CH_3)_3$

n	Formula	B.p. (p,mm Hg)	Cl, %		S, %		C, %		H, %	
			calc	found	calc	found	calc	found	calc	found
2	$Cl[(CH_3)_2SiO]_8Si(CH_3)_3$	197—199 (20)	5,05	4,95 5,02	36,06	35,92 35,90	32,53	32,82 32,70	8,19	8,22 8,17
3	$Cl[(CH_3)_2SiO]_{12}Si(CH_3)_3$	194—196 (3)	3,55	3,02 3,47	36,55	36,33 36,53	32,49	32,58 32,62	8,18	8,11 8,12
4	$Cl[(CH_3)_2SiO]_{16}Si(CH_3)_3$	233—235 (3)	2,74	2,50 2,27	36,85	36,30 36,13	32,47	32,95 32,78	8,17	8,11 8,18

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SYNTHESIS OF LIQUID 1, n-HEXAMETHYLPOLY (PHENYLETHYL) METHYLSILOXANES AND INVESTIGATION OF THEIR PROPERTIES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1615-1624, September, 1961
Original article submitted December 12, 1960

Liquid organosilicon polymers—polyorganosiloxanes—are widely used in the preparation of heat-stable lubricants, hydraulic fluids of low freezing point, liquid "compounds," etc. [1-4]. Certain valuable technical properties of liquid polyorganosiloxanes, particularly the low freezing point and small change of viscosity with temperature, are determined to a considerable degree by the low polarity of organosilicon polymers. However, the low polarity of organosilicon polymers often limits the possible fields of their application, especially where forces of cohesive interaction between molecules are important. In this respect it is of considerable interest to develop methods for synthesizing organosilicon polymers with polar groups in the organic radicals. A considerable amount of investigative work has been done on the synthesis of such polymers, but their properties have been considered only in a few works [5-10].

It was of interest to us to follow the change in the polar properties of liquid organosilicon polymers—1, n-hexamethylpoly (phenylethyl) methylsiloxanes—containing various polar substituents in the aromatic nucleus. To study the polar properties of the polymers investigated, we used the temperature dependence of viscosity and the activation energy of viscous flow, which characterize the polar properties of liquid polymers to a certain degree. The starting materials, used to synthesize the liquid polymers, were (phenylethyl) methyldichlorosilane, $C_6H_5C_2H_4(CH_3)SiCl_2$, (tolylethyl) methyldichlorosilane, $CH_3C_6H_4C_2H_4(CH_3)SiCl_2$, and chlorophenylethylmethyldichlorosilane, $ClC_6H_4C_2H_4(CH_3)SiCl_2$, whose syntheses we described earlier [11]. The liquid polymers were prepared through the joint hydrolysis of the indicated compounds with trimethylchlorosilane according to the following scheme:

$$RCH_2CH_2(CH_3)SiCl_2 + 2(CH_3)_3SiCl \xrightarrow{H_2O} (CH_3)_3SiO[Si(C_2H_4R)(CH_3)O]_nSi(CH_3)_3 + 2(n+1)HCl,$$

where $R = C_6H_5-$; $CH_3C_6H_4-$; ClC_6H_4-.

Depending on the proportions of trimethylchlorosilane and the difunctional compound, liquid polymers with various degrees of polymerization were isolated from the reaction mixture; their compositions and properties are given in Table 1.

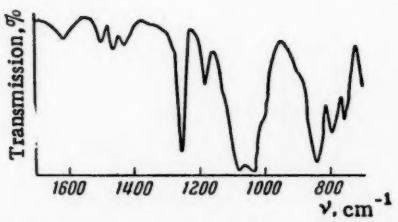


Fig. 1. IR spectrum of 1,4-hexamethyl-2, 3-di (phenylethyl)-2,3-dimethyltetrasiloxane (IV).

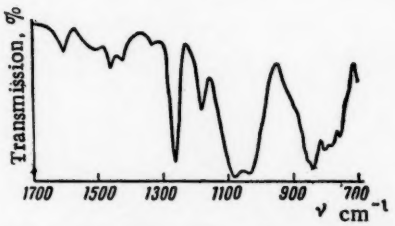


Fig. 2. IR spectrum of 1,4-hexamethyl-2, 3-di (tolylethyl)-2, 3-dimethyltetrasiloxane (V).

TABLE 1.

Substance no.	Substance	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	C, %		H, %		Si, %		Cl, %	
					found	calc.	found	calc.	found	calc.	found	calc.
I	$(CH_3)_3SiO[\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_4C_6H_5}{|}}{Si}}O]_1Si(CH_3)_3$	120—122(7)	1,4502	0,9098	55,33 55,42	55,16	9,30 9,33	9,25	24,46 24,18	25,77		
II	$(CH_3)_3SiO[\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_4C_6H_4CH_3}{|}}{Si}}O]_1Si(CH_3)_3$	141—142(10)	1,4572	0,9097	57,49 57,40	56,42	9,37 9,38	9,47	23,99 23,83	24,74		
III	$(CH_3)_3SiO[\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_4C_6H_4Cl}{|}}{Si}}O]_1Si(CH_3)_3$	140—141(7)	1,4573	0,9800	49,44 49,28	49,90	7,93 7,98	8,09	22,79 22,83	23,31	9,33 9,06	9,82
IV	$(CH_3)_3SiO[\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_4C_6H_5}{|}}{Si}}O]_2Si(CH_3)_3$	203—206(10)	1,4837	0,9778	58,92 58,99	58,72	8,27 8,27	8,62	21,81 21,81	22,86		
V	$(CH_3)_3SiO[\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_4C_6H_4CH_3}{|}}{Si}}O]_2Si(CH_3)_3$	211—216(10)	1,4859	0,9775	60,52 60,34	60,18	8,68 8,73	8,93	20,68 20,54	21,63		
VI	$(CH_3)_3SiO[\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_4C_6H_4Cl}{|}}{Si}}O]_2Si(CH_3)_3$	227—231(4)	1,4931	1,0713	51,26 51,20	51,49	6,98 6,87	7,20	19,16 19,10	20,05	11,92 12,26	12,67

TABLE 1, (Continued)

Substance no.	Substance	B.p., °C (p,mm Hg)	n_D^{20}	d_4^{20}	C. % found	C. % calc.	H. % found	H. % calc.	Si. %. found	Si. %. calc.	Cl. % found	Cl. % calc.
VII	$(CH_3)_3SiO[Si(C_2H_4C_6H_5)O]_6Si(CH_3)_3$ (CH₃)	282—300(4)	1,5079	1,0326	62,40 62,45	62,78	7,68 7,73	7,90	19,46 19,13	19,55		
VIII	$(CH_3)_3SiO[Si(C_2H_4C_6H_4CH_3)O]_6Si(CH_3)_3$ (CH₃)	282—296(4)	1,5059	1,0189	64,33 64,30	64,34	8,22 8,34	8,34	17,82 17,44	18,22		
IX	$(CH_3)_3SiO[Si(C_2H_4C_6H_5)O]_7Si(CH_3)_3$ (CH₃)	residue	1,5179	1,0552	62,64 62,39	63,16	7,78 7,64	7,83	18,98 19,20	19,24		
X	$(CH_3)_3SiO[Si(C_2H_4C_6H_4CH_3)O]_7Si(CH_3)_3$ (CH₃)	»	1,5163	1,0325	65,11 65,07	64,72	8,16 7,88	8,29	17,73 17,68	17,90		
XI	$(CH_3)_3SiO[Si(C_2H_4C_6H_4Cl)O]_5Si(CH_3)_3$ (CH₃)	»	1,5313	1,1784	53,18 53,24	52,99	6,29 6,12	6,36	16,40 16,42	16,99	15,77 15,80	15,33
XII	$[(C_6H_5C_2H_4)(CH_3)SiO]_3$	250—256(4)	1,5274	1,0649	65,92 65,78	65,81	7,47 7,47	7,36	16,87 16,70	17,08		
XIII	$[(C_6H_5C_2H_4)(CH_3)SiO]_4$	300—304(4)	1,5312	1,0757	65,87 35,92	65,81	7,32 7,35	7,36	16,97 17,01	17,08		

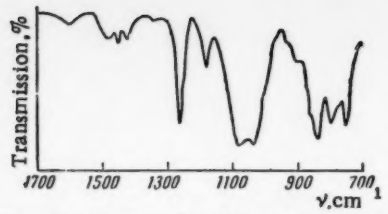


Fig. 3. IR spectrum of 1, 4-hexamethyl-2, 3-di (chlorophenylethyl)-2,3-dimethyltetrasiloxane (VI).

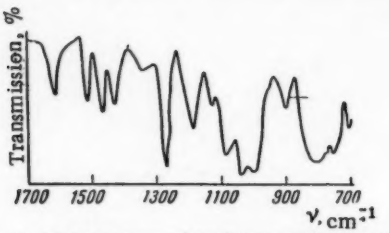


Fig. 4. IR spectrum of tri (phenylethyl) trimethylcyclotrisiloxane (XII).

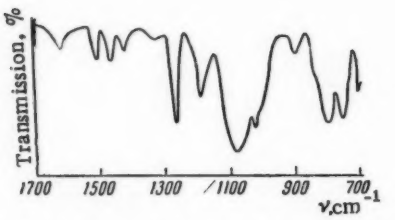


Fig. 5. IR spectrum of tetra (phenylethyl) tetramethylcyclotetrasiloxane (XIII).

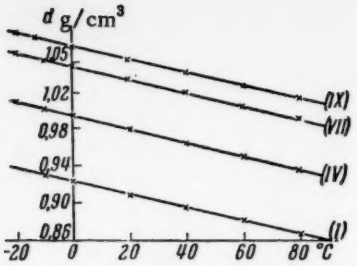
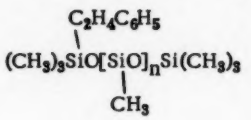


Fig. 6. Temperature dependence of specific gravity for



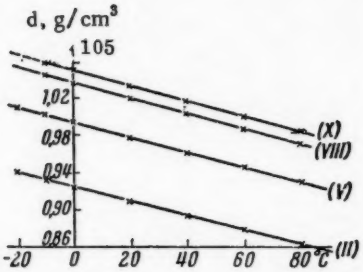


Fig. 7. Temperature dependence of specific gravity for

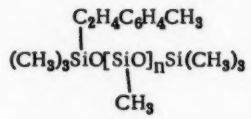


TABLE 2.

Substance no.	Viscosity in centipoises at the temperature							$K\frac{t°}{60°}$	Q, cal/M
	80°	60°	40°	20°	0°	−10°	−20°		
I	1,58	1,99	2,62	3,69	5,99	7,79	10,53	3,79	2,90
II	1,70	2,14	2,99	4,29	7,24	9,88	14,26	4,26	3,17
III	1,83	2,34	3,24	4,84	8,83	12,49	17,20	4,82	3,33
IV	3,27	4,62	7,11	12;64	30,87	52,19	1 3,72	9,65	4,63
V	3,82	5,58	9,33	18,78	57,39	107,07	273,92	15,02	5,45
VI	4,18	6,32	11,27	25,13	81,85	228,69	576,88	19,58	6,14
VII	6,95	10,75	19,28	40,89	161,90	690,27	2279,61	23,29	6,07
VIII	8,62	14,13	28,52	73,89	350,64	967,43	3638,00	40,68	7,36
IX	17,09	27,94	55,06	138,09	585,44	1515,15	4989,87	34,26	7,16
X	40,41	74,47	167,45	511,27	1887,82	5660,62	—	46,72	8,69
XI	56,48	112,49	298,00	1106,78	10078,87	—	—	178,5	10,19

The hydrolysis of (phenyl)methyldichlorosilane also gave cyclic polymers—tri (phenylethyl) trimethylcyclotrisiloxane $[C_6H_5C_2H_4(CH_3)SiO]_3$ and tetra (phenylethyl) tetramethylcyclotetrasiloxane $[C_6H_5C_2H_4(CH_3)SiO]_4$ according to the following equation:

$$nC_6H_5C_2H_4(CH_3)SiCl_2 + 2nH_2O \rightarrow [C_6H_5C_2H_4(CH_3)SiO]_n + 2nHCl$$

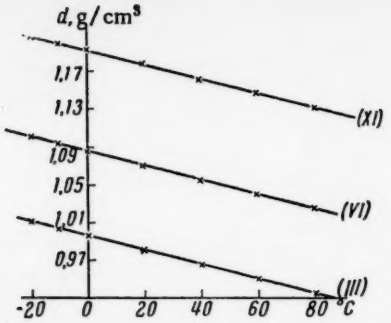
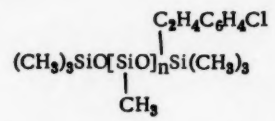


Fig. 8. Temperature dependence of specific gravity for



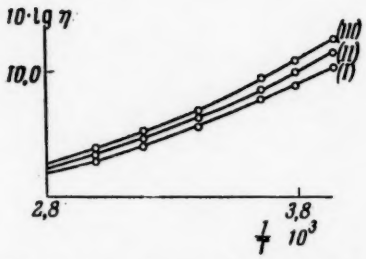


Fig. 9. Dependence of the logarithmic viscosity on the inverse absolute temperature for compounds (I), (II), and (III).

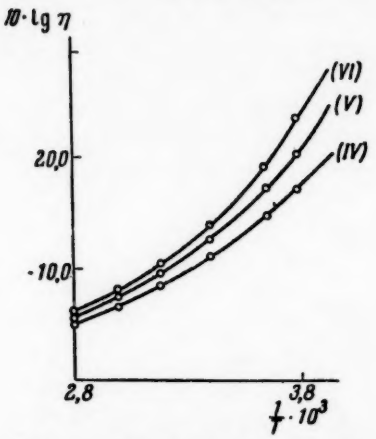


Fig. 10. Dependence of the logarithmic viscosity on the inverse absolute temperature for compounds (IV), (V), and (VI).

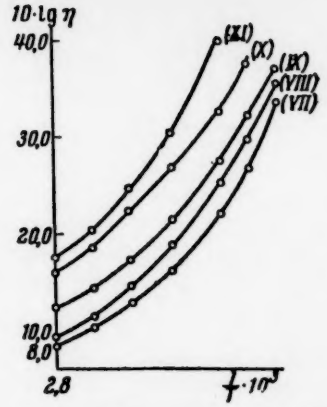


Fig. 11. Dependence of the logarithmic viscosity on the inverse absolute temperature for compounds (VII), (VIII), (IX), (X), and (XI).

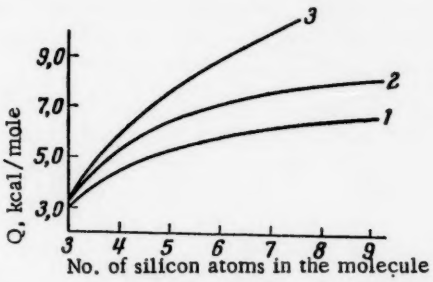


Fig. 12. Dependence of the activation energy of viscous flow on the number of silicon atoms in the molecule in polymers containing: 1) unsubstituted aromatics; 2) methyl groups in the aromatic nucleus; 3) chlorine.

The infrared spectra of some of the investigated compounds (IV, V, VI, XII, and XIII in Table 1) are shown in Figs. 1-5. The characteristic absorption bands for the Si—CH_3 grouping (1258 cm^{-1}) may be seen in Figs. 1-5; the characteristic absorption band in the 1030-1080 cm^{-1} region, corresponding to a siloxane bond in an open chain, may be seen in Figs. 1-3 (compounds IV, V, and VI). In the spectrum of compound (XII) (Fig. 4), which is a cyclic trimer, this absorption region is shifted to the right and lies in the interval 990-1040 cm^{-1}, whereas for compound (XIII) (cyclic tetramer) the absorption region of the siloxane bond gives a sharp maximum at 1080 cm^{-1}. It is interesting to note that in the 1375 cm^{-1} region, corresponding to symmetrical vibrations, of the C—CH_3 group in Fig. 1 there are no absorption bands. On this basis it may be assumed that the addition of an aromatic nucleus to vinylmethyldichlorosilane takes place in the β-position with the formation of β-substituted derivatives. The temperature dependence of the specific gravity for the investigated compounds is shown in Figs. 6, 7, and 8, whereas the dependence of the logarithmic viscosity for the investigated compounds on the inverse absolute temperature is shown in Figs. 9-11.

It is evident from the curves of Fig. 9, that in the temperature interval from 80 to 20°C the logarithmic viscosity for compounds (I), (II), and (III) is nearly a linear function of the inverse absolute temperature. On passing to lower temperatures the linearity is lost and the lines of Fig. 9 acquire an appreciable curvature.

The activation energy of viscous flow can be calculated for the linerar part of the curves in Fig. 9, proceeding from the Arrhenius equation

$$\eta = Ae^{\frac{Q}{RT}} + B$$

where A and B are constants, R is the gas constant, T is the absolute temperature, and Q is the activation energy of viscous flow. Data on the activation energy of viscous flow and the temperature coefficient of viscosity for the investigated compounds, are given in Table 2.

From the data, given in Table 2 and Fig. 9, it follows that the activation energy of viscous flow for the lower members of the homologous series (I, II, and III) depends only slightly on the presence of a polar group, although in all cases the replacement of a hydrogen atom in the nucleus by a methyl group or chlorine atom leads to a regular increase in the activation energy of viscous flow. This may be explained by the fact that in compounds (I, II, and III) the viscosity is more strongly affected by the terminal trimethylsiloxane groups, the specific content of which in the indicated compounds is very great in comparison with the specific content of the polar link. It is also interesting to note that for compound (III), containing a chlorine atom in the organic radical, the increase of viscosity in the low-temperature region is appreciably more rapid than for the low-polarity compounds (I) and (II). This indicates appreciable development of associative forces in the temperature interval from 20 to -20°.

On passing to the following group of members of a homologous series (compounds IV, V, and VI, Fig. 10), the activation energy of viscous flow is considerably increased in comparison with compounds (I), (II), and (III) in Fig. 9. This effect is due to the increase in the content of polar links in the molecules of compounds (V) and (VI) and the decrease in the effect of terminal trimethylsilyl groups in comparison with compounds (I), (II), and (III). In Fig. 10 it may be seen also that the curve for the chlorine-containing polymer (VI) is higher and appreciably steeper than the curves for the less polar compounds (IV) and (V). Here it may be noted further that at low temperatures the associative forces are much more pronounced for compound (VI) which has strongly polar, chlorine-containing organic radicals. This regularity is observed on investigation of the viscous properties of higher members of these homologous series (Fig. 11, curves VII-XI), for which the dependence of $\log \eta$ on $1/T$ is even more pronounced; especially for XI, which contains polar radicals.

The dependence of the activation energy of viscous flow on the number of silicon atoms in the investigated substances, is shown in Fig. 12. It may be seen from consideration of the curves, that the increase in the activation energy of viscous flow with the polymeric-chain length is most pronounced for chlorine-containing polymers (curve 3), less so for polymers containing methyl groups in the aromatic nucleus (curve 2), and least for polymers containing unsubstituted aromatic nuclei (curve 1). The data obtained agree well with those of Hurd [12] who found a similar regularity in the variation of Q with the number of silicon atoms for polydimethylsiloxanes with trimethylsiloxane end groups. On the basis of the observed regularity the investigated radicals may be arranged in the order of decreasing polar porperites as follows: $-C_2H_4C_6H_4Cl > -C_2H_4C_6H_4CH_3 > -C_2H_4C_6H_5$.

EXPERIMENTAL

The following compounds were used in the work: (phenylethyl)methyldichlorosilane, b.p. 90-92°C (5 mm), chlorine content 32.12%; (tolylethyl) methyldichlorosilane, b.p. 103-105°C (2 mm), chlorine content 30.51%; (chlorophenylethyl) methyldichlorosilane, b.p. 124-126°C (2 mm), alkali-titratable chlorine content 27.70%; trimethylchlorosilane, b. p. 58-59°C, chlorine content 33.27%.

1, 3-Hexamethyl-2-phenylethyl-2-methyltrisiloxane (I). Into a three-neck flask provided with a stirrer, dropping funnel, reflux condenser, and thermometer, 220 g of water and 55 g of toluene were put. The mixture was heated to 90-95°C, and a solution of 50 g (0.229 mole) of (phenylethyl) methyldichlorosilane and 59.53 g (0.546 mole) of trimethylchlorosilane in 55 g of toluene was added with vigorous stirring. After all the chloride mixture had been added, the reaction mass was stirred for 1.5 hr more at 80-90°C, cooled, washed to remove hydrochloric acid, dried with sodium sulfate, the solvent distilled off, and the residue fractionated in vacuo. In all there was obtained 65 g (87.2% of theory of a liquid reaction product, all of which distilled in the interval 116-131°C (7 mm). For the investigations a narrow fraction with b.p. 120-122°C (7 mm) was isolated, which corresponded in

composition to 1, 3-hexamethyl-2-phenylethyl-2-methyltrisiloxane; n_D^{20} 1.4502; d_4^{20} 0.9098. Found: C 55.33; 55.42; H 9.30; 9.33; Si 24.46, 24.18%. $C_{15}H_{30}Si_3O_2$. Calculated: C 55.16; H 9.25, Si 25.77%.

1, 4-Hexamethyl-2, 3-di (phenylethyl)-2,3-dimethyltetrasiloxane (IV). This was prepared by the method described above from 50 g (0.229 mole) of (phenylethyl) methyldichlorosilane, 29.76 g (0.273 mole) of trimethylchlorosilane, and 80 g of toluene. In all there was obtained 52 g (92% of theory) of a liquid which distilled in the interval 133-231°C (12 mm). For the investigations a fraction with b. p. 203-206°C (10 mm) was isolated, which corresponded in composition to 1, 4-hexamethyl-2, 3-di (phenylethyl)-2, 3-dimethyltetrasiloxane; n^{20}_D 1.4837; d_4^{20} 0.9778. Found: C 58.92; 58.99; H 8.27; 8.27; Si 21.81; 21.81%. $C_{24}H_{42}Si_4O_3$. Calculated: C 53.72; H 8.62; Si 22.86%.

1, 8-Hexamethyl-2,3,4,5,6,7-hexa (phenylethyl)-2,3,4,5,6,7-hexamethyloctasiloxane (VII). This was prepared by the method described above from 60 g (0.274 mole) of (phenylethyl)methyldichlorosilane, 21.79 g(0.199 mole) of trimethylchlorosilane, and 80 g of toluene. There was obtained 47 g of an organosilicon liquid which distilled in the temperature interval 130-310°C (4 mm). For the investigations a fraction with b.p. 282-300°C (4 mm) was isolated, which corresponded in composition to (VII); n_D^{20} 1.5079; d_4^{20} 1.0326. Found: C 62.40; 62.45; H 7.68; 7.73; Si 19.46; 19.13%. $C_{60}H_{90}Si_8O_7$. Calculated: C 62.78; H 7.90; Si 19.55%.

1, 9-Hexamethyl-2,3,4,5,6,7,8-hepta (phenylethyl)-2,3,4,5,6,7,8-heptamethylnonasiloxane (IX). This was prepared similarly from 60 g (0.274 mole) of (phenylethyl) methyldichlorosilane, 16.28 g (0.15 mole) of trimethylchlorosilane, and 80 g of toluene. There was obtained 49 g of a liquid which could not be distilled. To purify the product obtained, all substances boiling at temperatures up to 300°C (4 mm) were distilled from it. The residue, left after driving off, the volatile constituents, was used in the investigations; according to data of elementary analysis it corresponded to compound (IX); n_D^{20} 1.5179; d_4^{20} 1.0552. Found: C 62.64; 62.39; H 7.78; 7.64; Si 18.98; 19.20%. $C_{69}H_{102}Si_9O_8$. Calculated: C 63.16; H 7.83; Si 19.24%.

1,3-Hexamethyl-2-(tolylethyl)-2-methyltrisiloxane (II). This was prepared from 50 g (0.21 mole) of tolylethyl methyldichlorosilane, 56 g (0.51 mole) of trimethylchlorosilane, and 100 g of toluene. For the investigations a fraction with b.p. 141-142°C (10 mm) was isolated, which according to analytical data corresponded to compound (II); n_D^{20} 1.4572; d_4^{20} 0.9097. Found: C 57.49; 57.40; H 9.37; 9.38; Si 23.99; 23.83. $C_{16}H_{32}SiO_2$. Calculated: C 56.42; H 9.47; Si 24.74%.

1, 4-Hexamethyl-2,3-di(tolylethyl)-2, 3-dimethyltetrasiloxane (V). This was prepared from 56 g (0.24 mole) of (tolylethyl) methyldichlorosilane, 31 g (0.28 mole) of trimethylchlorosilane, and 100 g of toluene. For the investigations a fraction with b.p. 211-216°C (10 mm) was isolated, which according to analytical data corresponded to compound (V); n_D^{20} 1.4859; d_4^{20} 0.9775. Found: C 60.52; 60.34; H 8.68; 8.73; Si 20.68; 20.54%. $C_{26}H_{46}Si_4O_3$. Calculated: C 60.18; H 8.93; Si 21.63%.

1,8-Hexamethyl-2,3,4,5,6,7-hexa (tolylethyl)-2,3,4,5,6,7-hexamethyloctasiloxane (VIII). This was prepared from 50 g (0.21 mole) of (tolylethyl) methyldichlorosilane and 18.6 g (0.17 mole) of trimethylchlorosilane in a medium of 70 g of toluene. For the investigations a fraction with b.p. 282-296°C (4 mm) was isolated, which according to analytical data corresponded to compound (VIII); n_D^{20} 1.5059; d_4^{20} 1.0189. Found: C 64.33; 64.30; H 8.22; 8.34; Si 17.82; 17.44%. $C_{60}H_{102}Si_8O_7$. Calculated: C 64.34; H 8.34; Si 18.22%.

1, 9-Hexamethyl-2,3,4,5,6,7,8-hepta (tolylethyl)-2,3,4,5,6,7,8-heptamethylnonasiloxane (X). This was prepared from 60 g (0.25 mole) of (tolylethyl) methyldichlorosilane and 16.75 g (0.15 mole) of trimethylchlorosilane in a medium of 80 g of toluene. The liquid products formed could not be distilled in vacuo; therefore the liquid residue left after distilling off all products boiling at temperatures up to 300°C (4 mm), was used for the investigations. This residue, according to data of elementary analysis, corresponded to compound (X); n_D^{20} 1.5163; d_4^{20} 1.0325. Found: C 65.11; 65.07; H 8.16; 7.88; Si 17.73; 17.68. $C_{76}H_{116}Si_9O_8$. Calculated: C 64.72; H 8.29; Si 17.90%.

1, 3-Hexamethyl-2-(chlorophenylethyl)-2-methyltrisiloxane (III). This was prepared from 50 g (0.19 mole) of (chlorophenylethyl) methyldichlorosilane and 51.36 g (0.47 mole) of trimethylchlorosilane in a medium of 100 g of toluene. For the investigations a fraction with b.p. 140-141°C (7 mm) was isolated, which according to analytical data corresponded to (III); n_D^{20} 1.4573; d_4^{20} 0.9800. Found: C 49.44; 49.28; H 7.93; 7.98; Si 22.79; 22.83; Cl 9.33; 9.06%. $C_{15}H_{29}Si_3O_2$. Calculated: C 49.90; H 8.09; Si 23.31%.

1,4-Hexamethyl-2,3-di (chlorophenylethyl)-2,3-dimethyltetrasiloxane (VI). This was prepared from 50 g (0.19 mole) of (chlorophenylethyl)-methyldichlorosilane and 25.7 g (0.23 mole) of triethylchlorosilane in a medium of 75 g of toluene. For the investigations a fraction with b.p. 227-231°C (4 mm) was isolated, which according to

analytical data corresponded to (VI); n_D^{20} 1.4931; d_4^{20} 1.0713. Found: C 51.26; 51.20; H 6.98; 6.87; Si 19.16; 19.10; Cl 11.92; 12.26%. $C_{24}H_{40}Si_4O_3Cl_2$. Calculated: C 51.49; H 7.20; Si 20.05; Cl 12.67.

1, 7-Hexamethyl-2,3,4,5,6-penta (chlorophenylethyl)-2,3,4,5,6-pentamethylheptasiloxane (XI). This was prepared from 60 g (0.19 mole) of (chlorophenylethyl) methyldichlorosilane and 20.54 g of (0.19 mole) of trimethylchlorosilane in a medium of 80 g of toluene. The product obtained could not be distilled in vacuo, and therefore the residue, left after distilling off all products boiling at temperatures up to 260° (4 mm), was used for the investigations: this residue, according to data of elementary analysis, corresponded to compound (XI); n_D^{20} 1.5313; d_4^{20} 1.1784. Found: C 53.18; 53.24; H 6.29; 6.12; Si 16.40; 16.42; Cl 15.77; 15.80%. $C_{51}H_{73}Si_7O_6$. Calculated: C 52.99; H 6.36; Si 16.99; Cl 15.33%.

Tri (phenylethyl) trimethylcyclotrisiloxane and tetra (phenylethyl)-cyclotetrasiloxane (XIII). A solution of 100 g (0.45 mole) of (phenylethyl) methyldichlorosilane in 100 ml of ether was added, with stirring, to a mixture of 200 g of water and 100 ml of ether. During the hydrolysis the temperature was kept between 18 and 23°C. After all the chloride had been added, the mixture was stirred for 30 min more, and the organic layer was separated, washed until it gave a neutral reaction, and dried with sodium sulfate. After the solvent was driven off, all the remaining liquid (65 g) practically distilled in the temperature interval 250-305°C (4 mm). Fractions with b.pts. 250-256°C (4 mm) (triphenylethyltrimethylcyclotrisiloxane) and 300-305°C (4 mm) (tetraphenylethyltetramethylcyclotetrasiloxane) were isolated on refractionation. An elementary analysis was performed for each fraction, and the infrared spectra were taken.

Fraction with b.p. 250-256°C (4 mm), n_D^{20} 1.5274; d_4^{20} 1.0649. Found: C 65.92, 65.78; H 7.47, 7.47; Si 16.87, 16.70%; MR 142.53. $C_{27}H_{36}Si_3O_3$. Calculated: C 65.81; H 7.36; Si 17.08%; MR 142.35. Fraction with b.p. 300-304°C (4 mm), n_D^{20} 1.5312; d_4^{20} 1.0757. Found: C 65.87; 65.92; H 7.32; 7.35; Si 16.97; 17.01%; MR 190.04. $C_{36}H_{48}Si_4O_4$. Calculated: C 65.81; H 7.36; Si 17.08; MR 189.16.

The specific gravity of the liquids was determined by means of a 2-ml pycnometer at various temperatures. The samples were thermostated for 30 min before each determination. The data obtained are given in Figs. 6-8. The viscosities of all liquid samples were determined by standard methods with an Ostwald-Pinkevich viscometer. The data obtained are given in Table 2 and Figs. 9-11.

SUMMARY

1. The lower members of the homologous-polymer series of 1, n-hexamethylpoly(phenylethyl) methylsiloxanes were synthesized and their viscous properties studied.

2. When a hydrogen atom in the aromatic nucleus is replaced by a methyl group or chlorine atom, the activation energy of viscous flow increases, in correspondence with the increase in the polarity of the organic radicals, in the order $C_6H_5- < CH_3C_6H_4- < ClC_6H_4-$.

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REACTIONS OF BIS (TRIMETHYLSILOXY) DICHLOROSILANE WITH ALCOHOLS, PHENOLS, AND ALKOXIDES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1624-1629, September, 1961
Original article submitted February 2, 1961

Bis (trimethylsiloxy) dichlorosilane contains not only trimethylsiloxy groups attached to silicon, but also functional groups in the form of easily-hydrolyzable chlorine atoms. It is of interest to study the properties of this monomer in order to determine its prospects for the synthesis of polymers whose molecules contain siloxane chains, and also other polymers. However, owing to the absence of data on the reactivity of bis (trimethylsiloxy) dichlorosilane, it is difficult to estimate its possibilities. In the present work an attempt was made to study the reactions of bis (trimethylsiloxy) dichlorosilane with monohydric and dihydric alcohols, as well as mono-and dihydric phenols.

On investigating the reaction with monohydric alcohols according to the scheme

$$\begin{matrix}(CH_3)_3SiO\\(CH_3)_3SiO\end{matrix}\!\!>\!SiCl_2+2ROH\longrightarrow\begin{matrix}(CH_3)_3SiO\\(CH_3)_3SiO\end{matrix}\!\!>\!Si(OR)_2+2HCl \qquad (1)$$

methanol, ethanol, propanol-1, propanol-2,butanol-1, and 2-methylpropanol-1 were used. When the reaction was carried out by etherification of bis (trimethylsiloxy) dichlorosilane with a 10% excess of the corresponding absolute aliphatic alcohol without a hydrogen chloride acceptor, the reaction proceeded with intense spontaneous heating and hydrogen chloride evolution. However, no bis(trimethylsiloxy) dialkoxysilanes could be isolated from the reaction products. Apparently trimethylsiloxy groups attached to silicon are split out by hydrogen chloride, in the form of trimethylchlorosilane according to the equation

$$[(CH_3)_3SiO]_2SiCl_2+HCl\rightarrow(CH_3)_3SiO-\underset{\underset{OH}{|}}{SiCl_2}+(CH_3)_3SiCl \qquad (2)$$

The split-out trimethylchlorosilane is subsequently etherified by the excess alcohol, a trimethylalkoxysilane being formed. This hypothesis is confirmed by the fact that the products of reaction of bis (trimethylsiloxy) dichlorosilane with absolute ethanol gave a fraction, which was an azeotropic mixture of trimethylethoxysilane and ethanol, and a fraction, containing trimethylchlorosilane, from which hexamethyldisiloxane was isolated and characterized after hydrolysis. Thus the reaction, established earlier for trimethylsiloxy groups attached to titanium [1], also occurs in the case of trimethylsiloxy groups bound to a silicon atom. For reaction (2) to proceed, the presence of traces of moisture, which is formed in the reaction $ROH+HCl\rightleftharpoons RCl+H_2O$, is apparently very important. Since this reaction of bis (trimethylsiloxy) dichlorosilane with phenol gives bis (trimethylsiloxy) diphenoxysilane in 60.5% yield (Table 1).

To avoid side reactions caused by hydrogen chloride we used methods in which either the hydrogen chloride was neutralized or its formation was entirely precluded.

When bis (trimethylsiloxy) dichlorosilane was etherified with absolute ethanol in the presence of pyridine, bis (trimethylsiloxy) di-ethoxysilane was obtained in 68% yield. Treatment of bis (trimethylsiloxy) dichlorosilane with the corresponding sodium alkoxides according to the scheme

$$[(CH_3)_3SiO]_2SiCl_2+2RONa\rightarrow 2NaCl+[(CH_3)_3SiO]_2Si(OR)_2 \qquad (3)$$

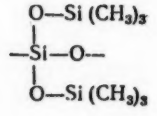
gave a series of bis (trimethylsiloxy) dialkoxysilanes; R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_4H_9. The physical properties of the compounds obtained are given in Table 1.

The reaction of bis (trimethylsiloxy) dichlorosilane with dihydric alcohols was studied in the case of ethanediol and butanediol-1,4. The reaction of bis (trimethylsiloxy) dichlorosilane with ethanediol gives an infusible, insoluble precipitate of composition C 17.66; H 4.98; Si 28.46 % and products boiling below 110° and consisting mainly of hexamethyldisiloxane, which was identified by the boiling point, refractive index, and specific gravity. Apparently the ethanediol is dehydrated during the reaction in accordance with the well-known scheme by which acetaldehyde or polyglycols are formed. In the presence of hydrogen chloride the resulting moisture promotes splitting-out of the trimethylsiloxy group and formation of a three-dimensional polymer and hexamethyldisiloxane according to the scheme

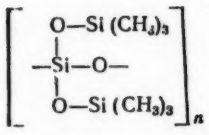
$$2\begin{matrix}(CH_3)_3SiO\\(CH_3)_3SiO\end{matrix}\!\!>SiCl_2+2H_2O \rightarrow 2\,(CH_3)_3SiOSiO_{1,5}+$$

$$+(CH_3)_3SiOSi\,(CH_3)_3+4\,HCl$$

On studying the reaction of bis (trimethylsiloxy) dichlorosilane with butanediol-1,4 it was found that the latter is almost quantitatively dehydrated to tetrahydrofuran, which was isolated, and characterized by the boiling point and refractive index. The water, evolved in the dehydration of butanediol-1,4, hydrolyzes the bis (trimethylsiloxy) dichlorosilane. However, the tetrahydrofuran, acting as a solvent in this case, apparently changes the course of the hydrolysis so that no significant splitting-out of trimethylsiloxy groups takes place, but rather the formation of products, distilling in vacuo in the 150-260° temperature range, and a small amount of liquid still-pot residue. The silicon content in the isolated fractions and still-pot residue remains practically unchanged and corresponds to that calculated for the elementary link

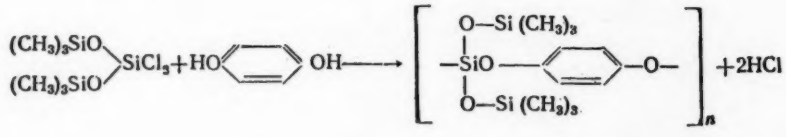


as a result of which it may be assumed that a mixture of cyclic or linear products of the formula



is formed in the given case. The properties of these products and other methods for synthesizing them are being studied.

The reaction of bis (trimethylsiloxy) dichlorosilane with dihydric phenols was investigated in the case of hydroquinone and 1,4- dihydroxydiphenylpropane. In the reaction of bis (trimethylsiloxy) dichlorosilane with hydroquinone in the solvent anisole or without solvent an elastic polymer is formed, which swells strongly in organic solvents. Data of elementary analysis correspond to the product obtained in the reaction

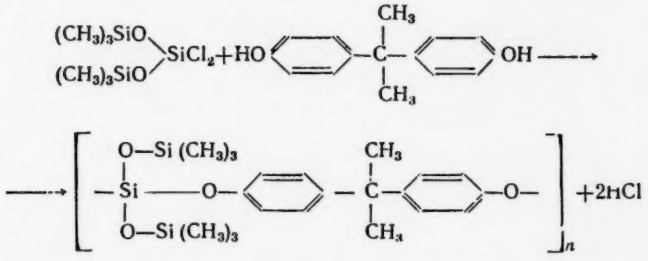


On long standing in air the polymer obtained becomes tacky, and then deliquesces. On boiling with aqueous ethanol it is readily hydrolyzed, hydroquinone being formed. Apparently the limited solubility of the product may be explained by secondary reactions of the quinone formed from the hydroquinone under the reaction conditions.

TABLE 1.

Formula	B. p., °C	n_D^{20}	d_4^{20}	MR calc.	MR found
$[(CH_3)_3SiO]_2Si(OC_4H_9\text{-}n)_2$	232—234	1,4003	0,8847	96,94	96,61
$[(CH_3)_3SiO]_2Si(OC_4H_9\text{-}i)_2$	225—227	1,3968	0,8757	96,94	96,88
$[(CH_3)_3SiO]_2Si(OC_3H_7\text{-}n)_2$	214—126	1,3943	0,8903	87,68	87,25
$[(CH_3)_3SiO]_2Si(OC_3H_7\text{-}i)_2$	202—203	1,3875	0,8752	87,68	87,31
$[(CH_3)_3SiO]_2Si(OC_2H_5)_2$	191—193	1,3870	0,8921	78,46	78,10
$[(CH_3)_3SiO]_2Si(OCH_3)_2$	174—175	1,3855	0,9155	69,16	68,84
$[(CH_3)_3SiO]_2Si(OC_6H_5)_2$	157—159 (3 mm)	1,4750	1,0330	106,59	106,85

The reaction of bis (trimethylsiloxy) dichlorosilane with 1.4'-dihydroxydiphenylpropane according to the scheme



leads to the formation of a polymer, which according to experimental analytical data corresponds to the reaction product. The polymer is a tough, sticky dark-brown mass which remains practically unchanged on standing in air and is readily soluble in toluene.

EXPERIMENTAL

The original bis (trimethylsiloxy) dichlorosilane was prepared through the reaction of hexamethyldisiloxane with silicon tetrachloride in an autoclave at 250° [2] and had the constants: b.p. 173°; d_4^{20} 1.0017; n_D^{20} 1.3983, Cl' 25.3%.

Etherification of Bis (trimethylsiloxy) dichlorosilane with Ethanol. Twenty g of bis (trimethylsiloxy) dichlorosilane in 20 ml of dry toluene was added dropwise at a temperature not over 20° to a mixture of 8.0 g of absolute ethanol and 11.4 g of dry pyridine. After heating at 110° for 5 hr the mixture was cooled, and the pyridine hydrochloride was filtered out, and washed twice on the filter with dry toluene. After distilling off the toluene up to 180°, 23.5 g of a product was obtained, which on fractionation gave fractions with b.pts. 180-190° (2.3 g), 190-200° (15.9 g – 68% of theory), and 200-215° (2.8 g) and a residue (2.4 g). The fraction with b.p. 190-200° was distilled twice, pure bis (trimethylsiloxy) diethoxysilane, b.p. 191-193°, being isolated. Found: C 40.07; 40.04; H 9.48; 9.34; Si 28.11; 28.60%. $C_{10}H_{28}Si_3O_4$ Calculated: C 40.57; H 9.16; Si 28.40%.

A 46 g quantity of bis (trimethylsiloxy) dichlorosilane was added dropwise to 20 g of absolute ethanol at 20-25°. To complete the reaction the mixture was heated for 3 hr at 50° and boiled for 2 hr at 75-80°. After heating, the product separated into two layers: upper (6.7 g) and lower (47.3 g). The upper layer consisted of ethanol saturated with HCl. The lower layer was fractionated in a column with 12 theoretical plates, the following fractions being obtained: I, b.p. 57-60°, 2.0 g; II, b.p. 60-67°, 4.2 g; III, 67-180°, 1.2 g; IV, b.p. 180-190°, 1.3 g; V, b.p. 190-210°, 0.8 g; VI, b.p. 210-230°, 1.2 g; residue 36.1 g. Fraction I had a Cl' content of 24.3%. After mixing with 2 g of water the upper layer was separated, dried with $CaCl_2$, and fractionated; there was isolated 0.8 g of a fraction with b.p. 99-101°; n_D^{20} 1.3764 (hexamethyldisiloxane, b.p. 100°; n_D^{20} 1.3760). Refractionation of fraction II gave 3.3 g of a 66-66.5° fraction with n_D^{20} 1.3735 (for the azeotropic mixture trimethylethoxysilane–ethanol; b.p. 66°, n_D^{20} 1.3729) [3].

Bis (trimethylsiloxy) di (n-butoxy) silane. A 1.4 g quantity of metallic sodium was dissolved in an excess of dry butanol[-1]. The unreacted butanol was distilled off in an oil bath by means of a water-jet pump until dry C_4H_9ONa was obtained. The residue was stirred with 30 ml of dry toluene, and 8.5 g of bis (trimethylsiloxy) dichlorosilane was added to the mixture. After heating for 2 hr the mixture was cooled and the NaCl precipitate centrifuged out. On fractionation the solvent was distilled off and there was collected 6.2 g of a fraction with b.p. 225-235° (57.5%), from which a pure product with b.p. 232-234° was isolated. Found: C 47.68; 47.57; H 10.16; 10.38; Si 23.78; 23.66%. $C_{14}H_{36}Si_3O_4$. Calculated: C 47.68; H 10.28; Si 23.87%.

Bis (trimethylsiloxy) diisobutoxysilane. The experiment was performed like the preceding. 2-Methylpropanol-1, 1.4 g of sodium, and 8.5 g of bis (trimethylsiloxy) dichlorosilane gave 8.6 g (82%) of a fraction with b.p. 225-232°, from which a fraction with b.p. 225-227° was isolated. Found: C 47.09; H 10.12; 10.14; Si 24.10; 24.35%. $C_{14}H_{36}Si_3O_4$. Calculated: C 47.68; H 10.28; Si 23.87%.

Bis (trimethylsiloxy) di (n-propoxy) silane. Similarly 2.13 g of sodium, propanol-1, and 12.7 g of bis (trimethylsiloxy) dichlorosilane gave 8.14 g (55%) of a fraction with b.p. 215-225°, from which a pure product with b.p. 214-216° was isolated. Found: C 44.18; 43.87; H 9.64; 9.68; Si 26.31; 26.13%. $C_{12}H_{32}Si_3O_4$. Calculated: C 44.4; H 9.93; Si 25.93%.

Bis (trimethylsiloxy) diisopropoxysilane. Similarly 2.13 g of sodium, propanol-2, and 12.7 g of bis (trimethylsiloxy) dichlorosilane gave 8.6 g (57%) of a fraction with b.p. 200-210°, from which a fraction with b.p. 202-230° was isolated. Found: C 44.95; 44.79; H 9.66; 9.69; Si 25.20; 25.30%. $C_{12}H_{32}Si_3O_4$. Calculated: C 44.4; H 9.33; Si 25.93%.

Bis (trimethylsiloxy) diethoxysilane. Absolute ethanol, 1.43 g of sodium, and 8.6 g of bis (trimethylsiloxy) dichlorosilane gave 6.1 g (61%) of a fraction with b.p. 190-200°.

Bis (trimethylsiloxy) dimethoxysilane. Twenty ml of absolute methanol, 1.43 g of sodium, and 8.6 g of bis (trimethylsiloxy) dichlorosilane gave 5.34 g (55%) of a fraction with b.p. 170-180°, from which a pure product with b.p. 174-175° was isolated. Found: C 36.11; 36.30; H 9.48; 9.34; Si 30.52; 80.77%. $C_8H_{24}Si_3O_4$. Calculated: C 35.78; H 8.99; Si 31.38%.

Bis (trimethylsiloxy) diphenoxysilane. To 10.5 g of molten phenol, 14.1 g of bis (trimethylsiloxy) dichlorosilane was added with stirring. The reaction began at 130°. The mixture, heated to 210°, was stirred for 5 hr. On fractionation at 3 mm there were isolated 4.76 g of unreacted phenol and 12.1 g (60.5%) of a fraction with b.p. 160-170° (3 mm). The latter was distilled twice, 3.8 g of a pure product with b.p. 157-159° (3 mm) being isolated. Found: C 54.91; 54.92; H 7.32; 7.24; Si 21.67; 21.96%. $C_{18}H_{28}Si_3O_4$. Calculated: C 55.05; H 7.18; Si 21.46%.

Reaction of Bis (trimethylsiloxy) dichlorosilane with Ethanediol. Ten g of bis (trimethylsiloxy) dichlorosilane was mixed with 2.24 g of ethanediol. On stirring in the cold the mixture became turbid. On heating to 100° for 2 hr a curdy precipitate formed. When the volatile products were distilled off, there was isolated 1.2 g of hexamethyldichlorosilane, b.p. 100-103°; n_D^{20} 1.3768; d_4^{20} 0.7641. According to literature data: b.p. 100°, n_D^{20} 1.3760, d_4^{20} 0.7658.

The precipitate was washed on the filter with toluene and dried to constant weight at 100° (3 mm): 6.2 g. Found: C 17.66; 17.55; H 5.02; 4.94; Si 28.59; 28.39%.

TABLE 2.

B. p. of fraction, °C	Yield, g	Si content, % calculated	Si content, % found*
180-200	1.4	37.85	37.27
			37.69
200-230	3.2	37.85	37.42
			37.49
230-260	2.7	37.85	37.28
			37.32
Residue	4.0	37.85	37.46
			37.64

* The Si content was calculated for the elementary link $[(CH_3)_3SiO]_2SiO$.

Reaction of Bis (trimethylsiloxy) dichlorosilane with Butanediol-1,4. Fifteen g of bis (trimethylsiloxy) dichlorosilane was stirred with 5.1 g of butanediol-1,4, the mixture being heated to 130°. After stirring for 5 hr two layers were formed: the lower (3.4 g), containing water, tetrahydrofuran, and HCl, and the upper (14.1 g). On fractionation of the upper layer there was isolated 1.3 g of tetrahydrofuran, b.p. 67°, n_4^{20} 1.408. The results of fractionating the residue at 3 mm and analyzing the fractions for silicon, are given in Table 2.

Reaction of Bis (trimethylsiloxy) dichlorosilane with Hydroquinone. A mixture of 3.96 g of hydroquinone and 10 g of bis (trimethylsiloxy) - dichlorosilane was refluxed,

with stirring, in an oil bath. HCl evolution began at 140°. On heating for 2 hr at 200° a polymer was formed, which became coiled up on the stirrer (13.3 g). Found: C 43.44; 43.50; H 6.73; 6.69; Si 26.38; 26.10%. $C_{12}H_{22}Si_3O_4$. Calculated: C 46.3; H 6.92; Si 26.67%.

Reaction of Bis(trimethylsiloxy)dichlorosilane with 1,4'-Dihydroxydiphenylpropane. A mixture of 2.8 g of bis (trimethylsiloxy)dichlorosilane and 2.0 g of 1,4'-dihydroxydiphenylpropane was stirred for 10 hr and simultaneously heated to 250° in an oil bath. After vacuum treatment (10 mm) 3.1 g of a viscous, dark-brown polymer, soluble in toluene, was obtained. Found: C 57.40; 57.22; H 7.62; 7.38; Si 18.86; 18.57%. $C_{21}H_{32}Si_3O_4$. Calculated: C 58.28; H 7.43; Si 19.48%.

1. The reactions of bis (trimethylsiloxy) dichlorosilane with monohydric alcohols and their alkoxides, as well as dihydric alcohols, phenol, and dihydric phenols, were studied.

2. Interaction with mono- and dihydric alcohols in the absence of hydrogen chloride acceptors is complicated by side reactions, whereas interaction with mono- and dihydric phenols proceeds normally.

3. Seven new bis (trimethylsiloxy) dialkoxy- (or -aryloxy) silanes of the type $[(CH_3)_3SiO]_2Si(OR)_2$, where R is Alk or Ar, were prepared.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE THERMAL DECOMPOSITION OF ADDUCTS OF ABIETIC ACID AND ITS ESTERS WITH MALEIC ANHYDRIDE

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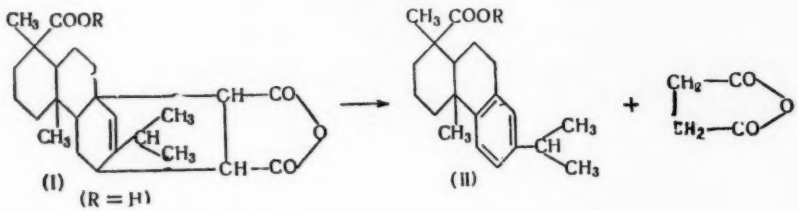
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1630-1635, September, 1961
Original article submitted February 26, 1961

As is well know, abietic acid when heated with maleic anhydride gives an adduct corresponding in structure to the adduct of maleic anhydride with levopimaric acid (I) [1].



As early as 1932, one of us [2] had noted that succinic anhydride was liberated in the thermal decomposition of (I). The thermal decomposition reaction was not investigated in detail. It could be assumed that in the thermal decomposition of the adduct (I), in addition to succinic anhydride, the formation of dehydroabietic acid (II) or the products of its further decomposition must take place.

The object of the present investigation was to study the products of the thermal decomposition of the adduct (I) and the adducts of maleic anhydride with esters of abietic acid (I, R = CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9). The thermal decomposition was carried out in a glass retort at 300-360°. In all cases, succinic acid was isolated. Thermal decomposition of the adduct (I) (R = H) gave dehydroabietic acid with m.p. 168 - 170°, $[\alpha]_D$+62.5° (alcohol), in a yield of 48% of theory. From its constants and ultraviolet spectrum (Fig. 1) it corresponded to dehydroabietic acid [3]. In addition to the dehydroabietic acid, a hydrocarbon fraction was obtained in the thermal decomposition of the adduct (I) from which two hydrocarbons (A and B) were isolated (yield 58.9% of theory) by chromatography on alumina. A: b.p. 197-200° (15-16 mm); d_4^{20} 0.9765; n_D^{20} 1.5342; $[\alpha]_D$+90.5° (methanol); + 92.1° (benzene); 67.1% of the hydrocarbon fraction. The ultraviolet spectrum is given in Fig. 2, curve 2. B: b.p. 194 - 197° (15 mm); d_4^{20}1.0345; n_D^{20} 1.5685; $[\alpha]_D$+33.5° (benzene), +17.5° (chloroform); 28.9% of the hydrocarbon fraction. The ultraviolet spectrum is given in Fig. 2, curve 3. The hydrocarbon A did not decolorize a chloroform solution of bromine. Hydrocarbon B showed the presence of a single double bond on titration with bromine according to MacIlhiney [4].

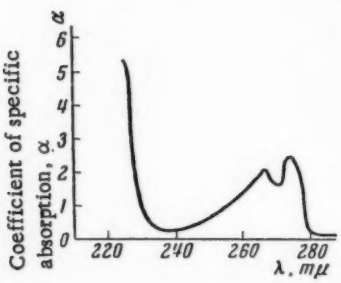
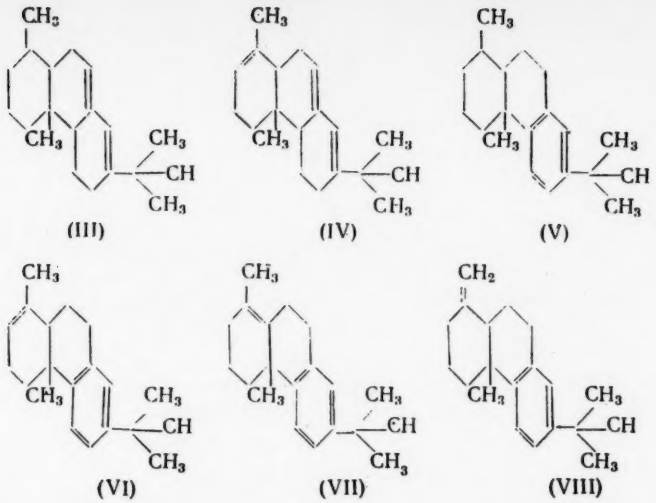


Fig. 1. Ultraviolet absorption spectrum of dehydroabietic acid

On increasing the temperature of thermal decomposition of the adducts (I) to 360°, the yield of hydrocarbons increases to 65-68% and the yield of dehydroabietic acid falls to 25-28%. At a temperature of the thermal decomposition of the adduct of 360-395°, the yield of hydrocarbon fraction falls to 50%. No dehydroabietic acid was isolated under these conditions.

On decarboxylating abietic acid by heating, the evolution of CO_2, CO, H_2, and CH_4 [5] takes place and a mixture of hydrocarbons to which structures (III) and (IV) are assigned are formed.



(III) (IV) (V)

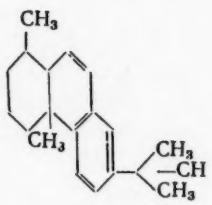
(VI) (VII) (VIII)

In the thermal decomposition of dehydroabietic acid or the adduct (I), the formation of hydrocarbons (V), (VI), (VII), and (VIII) might be expected as a result of decarboxylation. In fact, on distilling free dehydroabietic acid at 3-5 mm, about 40% of the hydrocarbons A and B are obtained; in this case, 75-80% of the hydrocarbons consists of hydrocarbon B.

In 1950, Brossi, Gutmann, and Jeger [6], in the thermal decomposition of the tertiary diphenyl carbinol obtained by the action of phenylmagnesium bromide on the methyl ester of dehydroabietic acid, obtained a mixture of hydrocarbons of saturated and unsaturated character from which the saturated hydrocarbon was isolated by chromatography. They assigned structure (V) to this hydrocarbon. The unsaturated hydrocarbons, in the opinion of these authors, consisted of a mixture of (V), (VI), and (VIII). A comparison of the constants of hydrocarbon A with the contents of Brossi, Gutmann, and Jeger's saturated hydrocarbon [b.p. 113° (0.1 mm); n_D^{20} 1.5400; $[\alpha]_D$+92° (methanol)] and of its uv spectrum with the uv spectrum given by Brossi, Gutmann and Jeger (Fig. 2, curves 1 and 2; see also [7]) showed that they were close to one another. Thus, it must be considered that hydrocarbon A has the structure (V).

The constants of fraction B and its uv spectrum differ considerably from the constants and uv spectrum of the mixture of (VI), (VII), and (VIII) given by Brossi, Gutmann and Jeger [b.p. 120-130° (0.05 mm); n_D^{20} 1.551; $[\alpha]_D$+130° (methanol)]. The hydrocarbon (VIII) was obtained by Zeiss and Martin [8] and had b.p. 73-78° (0.01 mm); n_D^{25} 1.5500; $[\alpha]_D$ +195.5 (1,1-dichloroethane). Its $[\alpha]_D$ differs considerably from that of fraction B.

Perold and Jeger [7], by the decomposition of the chloride of dehydroabietic acid in the presence of copper powder, obtained a hydrocarbon with b.p. 117-120° (0.02 mm); $[\alpha]_D$+11° (chloroform), and the uv spectrum of Fig. 2, curve 4, to which they assigned, on the basis of an infrared spectrum characteristic for styrene derivatives, the structure (IX) of stereoisomeric hydrocarbons. The authors explained the formation of (IX) by the isomerization of the compound (VIII) formed initially. Comparison of the absorption spectrum of fraction B with the absorption spectrum of (IX) shows that they are very close to one another which permits the assumption to be made that



(IX)

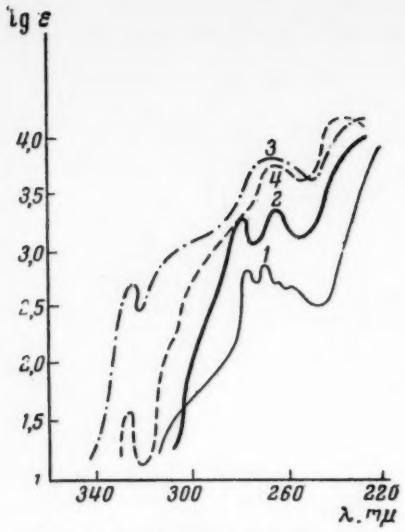


Fig. 2. Ultraviolet absorption spectra: 1) the hydrocarbon $C_{19}H_{28}$ (V) [6]; 2) obtained by us for hydrocarbon A; 3) obtained by us for hydrocarbon B; 4) the hydrocarbon $C_{19}H_{26}$ (IX) [7].

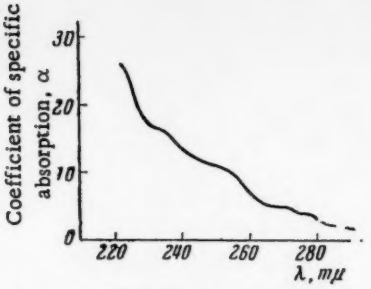


Fig. 3. Ultraviolet absorption spectrum of propyl dehydroabietate.

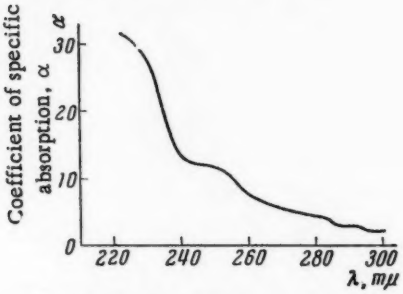


Fig. 4. Ultraviolet absorption spectrum of butyl dehydroabietate.

a mixture of the stereoisomeric hydrocarbons (IX) predominates in fraction B. A supplementary, more detailed investigation is required for the structures of the hydrocarbons of fractions A and B to be established definitively.

Thermal decomposition of the adducts of esters of abietic acid with maleic anhydride (I), where R= $-CH_3$, $-C_2H_5$, $-C_3H_7$, and $-C_4H_9$, was carried out under similar conditions, (320-360°). In all cases, succinic anhydride was isolated. In the case of the decomposition of the adducts of methyl and ethyl abietates with maleic anhydride, the decomposition led to hydrocarbons. In addition, dehydroabietic acid was isolated, and, in the case of the adduct with methyl abietate, a small amount of methyl dehydroabietate. In the decomposition of the adducts with propyl and butyl abietates, the corresponding esters of dehydroabietic acid (II) (R= $-C_3H_7$, $-C_4H_9$) were isolated with a yield of 70-80%. The ultraviolet spectra are given in Figs. 3 and 4. The propyl and butyl esters of dehydroabietic acid have not previously been described in the literature.

Thus, on the basis of all that has been mentioned, it is possible to conclude that the thermal decomposition of the adducts of abietic acid and propyl and butyl abietates with maleic anhydride at 320-360° may be used for the production of dehydroabietic acid and its propyl and butyl esters, respectively (in yields of 48, 77.9, and 70.8% of theory, respectively).

EXPERIMENTAL PART

Production of the adduct of ethyl abietate with maleic anhydride. A mixture of 10 g of ethyl abietate [b.p. 204-207° (4 mm); d_4^{20} 1.029; n_D^{20} 1.5297; $[\alpha]_D$ -26.5°] and 4 g of freshly-distilled maleic anhydride was heated in a sealed glass tube for 10-12 hours at 150-160°. The glass-like mass formed was first treated with petroleum and then recrystallized from methyl alcohol. A yield of 6 g of the adduct of ethyl abietate with maleic anhydride (I) (R=C_2H_5) in the form of a white microcrystalline mass was obtained. After two recrystallizations from methyl alcohol: b.p. 152-154°; $[\alpha]_D$ -36.5° (chloroform). Found: C, 73.12; H, 8.57%. $C_{26}H_{36}O_5$. Calculated: C, 72.89; H, 8.41%; mol.wt. 428.

Production of the adduct of propyl abietate with maleic anhydride. A mixture of 15 g of propyl abietate [b.p. 237-240° (4 mm); d_4^{20} 1.011; n_D^{20} 1.5243; $[\alpha]_D$ -44.5° (alcohol)] and 6 g of freshly-distilled maleic anhydride was heated in a sealed glass tube for 10-13 hours at 150-160°. On treating the glass-like mass obtained with cold

methyl alcohol, 13.5 g (70% of theory) of a white powdery substance separated; after recrystallization from hot methyl alcohol it formed white microcrystals of (I) (R=C_3H_7) with b.p. 140-142°; $[\alpha]_D$ -42.5° (chloroform). Found, C, 73.1; H, 8.46. $C_{27}H_{38}O_5$. Calculated: C, 73.3; H, 8.59%; mol. wt. 442.

Production of the adduct of butyl abietate with maleic anhydride. A mixture of 10 g of butyl abietate [b.p. 247-250° (3 mm); d_4^{20} 1.010; n_D^{20} 1.5223; $[\alpha]_D$ -45° (alcohol)] with 4 g of freshly-distilled maleic anhydride was heated in a sealed glass tube for 12-13 hours at 150-160°. On treating the brown glassy mass formed with cold methyl alcohol, 10.2 g (80% of theory) of a white amorphous powder (I) (R=C_4H_9) was obtained. On recrystallization from methyl alcohol, a white microcrystalline mass was obtained: b.p. 136-138°; $[\alpha]_D$ -44.5° (chloroform). Found: C, 73.81; H, 8.85%. $C_{28}H_{40}O_5$. Calculated: C, 73.68; H, 8.77%; mol. wt. 456.

Thermal decomposition of the adduct of abietic acid with maleic anhydride (I) (R=H). Twenty grams of the adduct of abietic acid with maleic anhydride (I) (R=H) [b.p. 223-225°; $[\alpha]_D$ -21.5° (alcohol)] was heated in a retort at 300-320° for 10 hours. The sublimation of succinic anhydride (m.p. 119-120°) began at a temperature of 308-310°; the yield was 4 g (80% of theory). The first crystals of succinic anhydride began to appear at 280°; at 320° an oily liquid began to separate (7.5 g). The amount of succinic anhydride produced was determined by titration with 0.5 N NaOH. The residue in the retort was extracted with ether and distilled in vacuum after the removal of the ether: b.p. 230-234° (5 mm); 198-202° (1.5-2 mm). A yield of 7.2 g (48% of theory) of dehydroabietic acid (II) (R=H) was obtained. After recrystallization from n-hexane it had: m.p. 168-170°, $[\alpha]_D$+62.5° (alcohol). The uv spectrum of the dehydroabietic acid which we obtained is identical with the spectrum of dehydroabietic acid found in the literature [3]. Literature data: m.p. 171-173°; $[\alpha]_D$+62.5° (alcohol). The liquid fraction was dissolved in ether, washed with dilute NaOH solution and, after drying with calcined Na_2SO_4, distilled in vacuum (7.5g): b.p. 152-154° (1.5-2 mm); 195-198° (15-16 mm); n_D^{20} 1.5527; $[\alpha]_D$+ 35.5° (benzene).

For separating the mixture of hydrocarbons, the liquid fraction (7.4 g) was chromatographed on alumina (activity III according to Brockmann [9]). Petroleum ether (40-60°) eluted 5.1 g of a colorless hydrocarbon A; b.p. 197-200° (15-16 mm); d_4^{20} 0.9765; n_D^{20} 1.5342; $[\alpha]_D$+92.1° (benzene); +90.5° (methanol). Its uv spectrum is given in Fig. 2, curve 2. When a solution of bromine was added to a solution of the hydrocarbon in carbon tetrachloride, no decolorization of the bromine solution was observed, which indicates the absence of double bonds. Hydrocarbon B (II) (2.2 g) was eluted with a mixture of ether and petroleum ether (1:4). It is a yellowish oil with a blue-violet fluorescence in reflected light, with b.p. 194-197° (15 mm); n_D^{20} 1.5685; d_4^{20} 1.0345; $[\alpha]_D$+33.5° (benzene); +17.5° (chloroform). The number of double bonds determined by MacIlhiney's method [4] confirms the presence of a single double bond in this hydrocarbon (0.8430 g of the substance added an amount of bromine equivalent to 0.8420 g of iodine, and 0.8430 g of the substance should have added an amount of bromine equivalent to 0.8430 g of iodine). The uv spectrum of the second hydrocarbon is given in Fig. 2, curve 3.

On distilling dehydroabietic acid obtained by the method of Dupont [10] at 3-5 mm, about 40% of the above hydrocarbons was isolated, the greater part consisting of the second hydrocarbon (75-80%): b.p. 194-197° (15 mm); d_4^{20} 1.0345; n_D^{20} 1.5685; $[\alpha]_D$ +33.5° (benzene); +17.5° (chloroform).

On raising the temperature of the thermal decomposition of the adduct with abietic acid to 360°, the yield of the hydrocarbon fraction increased to 65-68% and the yield of succinic anhydride to 90%, while the yield of dehydroabietic acid fell to 25-28%. At a temperature of thermal decomposition of 360-395°, the yield of succinic anhydride increased to 95%, but the yield of hydrocarbon fraction fell to 50%. Dehydroabietic acid was not isolated under these conditions. An undistillable residue remained in the retort.

Thermal decomposition of the adduct of methyl abietate with maleic anhydride (I) (R= $-CH_3$). Ten grams of the adduct (I) (R= $-CH_3$) of methyl abietate with maleic anhydride [m.p. 213-214°; $[\alpha]_D$ -26.5° (chloroform)] was heated in a retort at 320-360° for 12-15 hours. A yield of 2 g (83.1% of theory) of succinic anhydride (m.p. 119°) and 1.05 g (13.1% of theory) of methyl dehydroabietate (II) (R= $-CH_3$) – b.p. 206-209° (5-5.5 mm); 238-243° (24-25 mm); n_D^{20} 1.5396; $[\alpha]_D$ +56.5° (alcohol) – was obtained. Literature data [11]: m.p. 56-60°; $[\alpha]_D$+59° (alcohol). Found: C, 80.05; H, 9.46%. $C_{21}H_{30}O_2$. Calculated: C, 80.25; H, 9.52%; mol. wt. 314.

In addition, 2 g (33% of theory) of hydrocarbon B was isolated: b.p. 194-197° (15 mm); n_D^{20} 1.5685; d_4^{20} 1.0344; $[\alpha]_D$ +33.5° (benzene); together with 2.5 g of hydrocarbon A (40% of theory): b.p. 197-200° (15-16 mm); d_4^{20} 0.9765; n_D^{20} 1.5342; $[\alpha]_D$ +92.1° (benzene), +90.5° (methanol).

The hydrocarbon fraction was separated by a chromatographic method similar to that described above. The residues in the retort yielded dehydroabietic acid (0.2 g): m.p. 168-170° (from n-hexane) and $[\alpha]_D$ +62.0° (alcohol).

Methyl dehydroabietate and the hydrocarbons distilled over during the thermal decomposition and were separated by vacuum distillation.

Thermal decomposition of the adduct of ethyl abietate with maleic anhydride (I) (R= $-C_2H_5$). Four grams of the adduct of ethyl abietate with maleic anhydride – m.p. 152-154°; $[\alpha]_D$ -36.5° (chloroform) – were heated in a retort at 320-360° for 10-12 hours. The products isolated from the decomposition were: 0.75 g (80.6% of theory) of succinic anhydride (m.p. 119° after washing with ether); 0.8 g of hydrocarbon B (33.2% of theory); b.p. 194-197° (15 mm); n_D^{20} 1.5685 d_4^{20} 1.0345; $[\alpha]_D$ +33.5° (benzene); and 0.6 g of hydrocarbon A (24.9% of theory): b.p. 197-200° (15-16 mm); d_4^{20} 0.9765; n_D^{20} 1.5342; $[\alpha]_D$ +92.1° (benzene). In addition, 0.6 g (21.4% of theory) of dehydroabietic acid was isolated from the residues in the retort: b.p. 203-205° (1.5-2 mm); m.p. 168-170° (from n-hexane); $[\alpha]_D$ +60.5° (alcohol).

Thermal decomposition of the adduct of propyl abietate with maleic anhydride (I) (R= $-C_3H_7$). The adduct [m.p. 140-142°; $[\alpha]_D$ -32.5° (chloroform)] was heated in a retort in a metal bath at 320-360° for 10-12 hours. A yield of 1.9 g of succinic anhydride (82.5% of theory) with m.p. 119° was isolated together with 6 g of propyl dehydroabietate (77.9% of theory): b.p. 204-206° (3 mm); n_D^{20} 1.5218; d_4^{22} 1.0382; $[\alpha]_D$ +36.5° (alcohol). The uv absorption spectrum of propyl dehydroabietate (II) (R= $-C_3H_7$) is shown in Fig. 3. Found: C, 81.03; H, 10.03%. $C_{23}H_{34}O_2$. Calculated: C, 80.70; H, 9.94%; mol.wt. 342.

Saponification of the alkyl dehydroabietates. The saponification of methyl, propyl, and butyl dehydroabietates was carried out by boiling aqueous solutions of the esters with an aqueous-alcoholic solution of KOH under reflux for 10 hours. The aqueous alcoholic solutions were then acidified and extracted with ether. The ethereal extract was dried with calcined Na_2SO_4. After distilling off the ether, dehydroabietic acid was isolated in all cases: m.p. 168-170° (n-hexane), $[\alpha]_D$ +62° (alcohol).

Thermal decomposition of the adduct of butyl abietate with maleic anhydride (I) (R= $-C_4H_9$). Ten grams of the adduct of butyl abietate with maleic anhydride – m.p. 136-138°; $[\alpha]_D$ -37.5° (chloroform) – was heated in a retort at 320-360° for 10-12 hours. As a result of the thermal decomposition, 1.8 g of succinic anhydride (81.6% of theory) was isolated, together with 5.5 g of butyl dehydroabietate (70.8% of theory) (II) (R= $-C_4H_9$) with b.p. 203-205° (3.5-4 mm); d_4^{22} 1.0377; n_D^{20} 1.5227; $[\alpha]_D$ +27.5 (alcohol). Its uv spectrum is shown in Fig. 4. Found: C, 81.21; H, 10.22%. $C_{24}H_{36}O_2$. Calculated: C, 80.89; H, 10.11%; mol. wt. 356.

SUMMARY

1. Adducts of ethyl, propyl, and butyl abietates with maleic anhydride have been obtained.

2. The thermal decomposition of the adducts of abietic acid and methyl, ethyl, propyl, and butyl abietates with maleic anhydride leads to dehydroabietic acid and the corresponding dehydroabietates, the decarboxylation of which leads to the formation of hydrocarbons.

3. The thermal decomposition of the adducts of abietic acid and propyl and butyl abietates may be used for the preparation of dehydroabietic acid and propyl and butyl dehydroabietates, respectively.

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AN INVESTIGATION IN THE FIELD OF THE STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 42. SYNTHESIS AND CATALYTIC HYDROGENATION OF 7-METHOXY-1,2-bis-(HYDROXYMETHYL)-HEXAHYDROPHENANTHRENES

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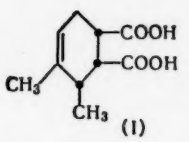
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1636-1640, September, 1961
Original article submitted January 20, 1961

We showed earlier that the catalytic hydrogenation of cis-cis-3,4-dimethyl-Δ^4-cyclohexene-1,2-dicarboxylic acid (I) [1], cis-syn-Δ^4-octalin-1,2-dicarboxylic acid (II) [2], and cis-syn-7-methoxy-1, 2, 3, 9, 10, 10a-hexahydrophenanthrene-1,2-dicarboxylic acid (III) [3], and also that of their derivatives (anhydrides, diesters, monoesters), takes place with spatial selectivity. In all these cases, the hydrogen adds from the side of the ring opposite to that of the carboxyl groups, leading to isomers possessing cis-syn-cis (cis-cis-cis-) -configurations. The hydrogenation of cis-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene-1,2-dicarboxylic acid (IV), its anhydride and its dimethyl ester [3], over 30% $Pd/SrCO_3$ [4] also proceeds stereospecifically with the formation of the corresponding compound of the cis-syn-cis series.



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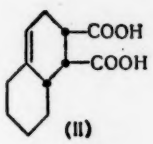

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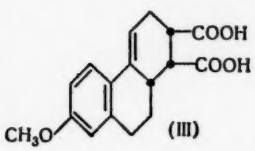

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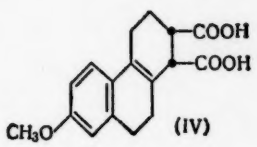
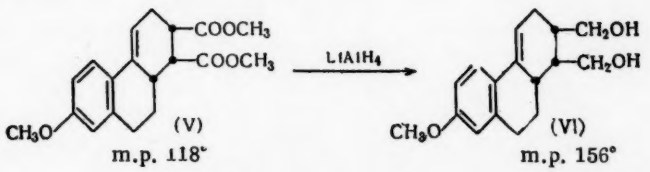
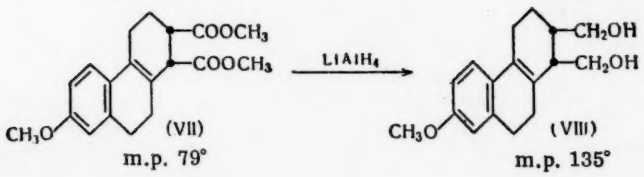


(IV)

To study further the dependence of the stereospecificity of hydrogenation on the nature of the screening groups, it appeared to us to be of interest to ascertain the spatial direction of the catalytic hydrogenation of the glycols readily obtained by the reduction of the dimethyl esters of the unsaturated acids (III) and (IV) with lithium aluminium hydride. Moreover, these glycols might subsequently be used for the stereospecific synthesis of analogs of the 16-ketosteroids, which have an interest of their own.



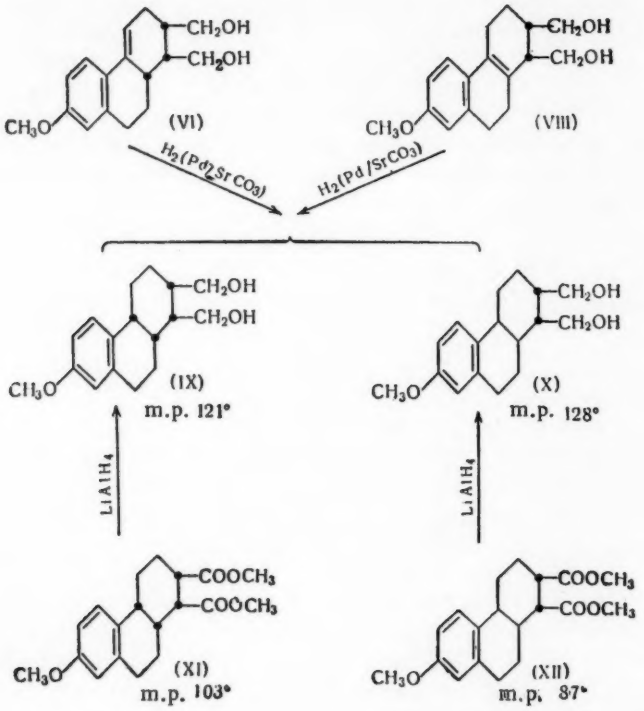
(V) m.p. 118° (VI) m.p. 156°



(VII) m.p. 79° (VIII) m.p. 135°

The reduction of the cis-syn diester (V) with aluminum anhydride takes place very readily and leads, with a good yield, to the corresponding cis-syn glycol (VI) with m.p. 155°, giving a diacetate with m.p. 72° on boiling with acetic anhydride. Similar reduction of the cis diester (VII) yielded the cis glycol (VIII), melting at 135°, treatment of which with acetyl chloride led to a diacetate with m.p. 85°. The same diacetate was formed quantitatively as a result of double-bond displacement in the cis-syn glycol (VI) when it was boiled with acetyl chloride for 15 minutes. Such isomerization of a double bond apparently proceeds under the influence of the hydrogen chloride present in the reaction mixture [3].

Hydrogenation of the cis-syn glycol (VI) in dioxane over 30% $Pd/SrCO_3$ [4] proceeds relatively rapidly with the absorption of one mole of hydrogen, but it leads not to a definite individual glycol but to a mixture of, apparently, equal amounts of the two possible geometrical isomers (IX) and (X). By fractionally crystallizing this mixture we were able to isolate the pure cis-syn-cis glycol (IX) in a yield of only ~10%; it had m.p. 121° and was also characterized in the form of its diacetate. Its configuration is shown by the fact that it is formed from the dimethyl ester of cis-syn-cis-7-methoxy octahydrophenanthrene-1,2-dicarboxylic acid (XI) with a yield of about 94% on reduction with lithium aluminum hydride.



The hydrogenation of the cis glycol (VIII) likewise proceeds nonselectively, leading to a mixture of the same geometrical isomers, from which only the cis-anti-cis glycol (X), melting at 128°, could be isolated in small yield. The configuration of the cis-anti-cis glycol (X) is shown rigidly by its formation from the dimethyl ester of cis-anti-cis-7-methoxy-1, 2, 3, 4, 4a, 9, 10, 10a-octahydrophenanthrene-1,2-dicarboxylic acid (XII) on reduction with lithium aluminium hydride.

Thus, it has been shown that on replacing the carboxyl (or methoxycarbonyl) groups in cis-syn-Δ^4- and cis-$\Delta^{4a(10a)}$-hexahydrophenanthrene-1,2-dicarboxylic acids (or their esters) by hydroxymethyl groups, spatial selectivity of the hydrogenation of the double bonds in these compounds is completely lacking. The addition of the hydrogen takes place from both possible sides of the ring, leading to a mixture of the two geometrical isomers in approximately equal amounts. The results obtained show that the hydroxymethyl groups possess a less pronounced screening effect than the carboxyl groups, which may be due not only to their smaller spatial dimensions but, apparently also to their electrostatic properties.

EXPERIMENTAL PART*

The cis-syn glycol (VI). To 40 ml of a 0.7 M ethereal solution of lithium aluminium hydride, a solution of 3.0 g of the cis-syn diester (V) [3] in 25 ml of absolute dioxane was added with stirring at a such a rate that the ether boiled gently (15 min). The mixture was stirred and boiled for 1 hour. The excess of lithium aluminium hydride was decomposed by the addition of ethyl acetate. Then the mixture, cooled with ice, was treated with 50 ml of 10% sulfuric acid; the crystalline residue which separated was filtered off, washed with water to neutrality to Congo red, and dried in air. A yield of 2.35 g (92%) of the cis-syn glycol (VI) with m.p. 142-145° was obtained; on crystallization from dioxane it separated in the form of fine needles melting at 155-156°. Found: C, 74.35; 74.31; H, 8.09; 8.16%. $C_{17}H_{22}O_3$. Calculated: C, 74.42; H, 8.08%.

A mixture of 0.08 g of the cis-syn glycol (VI) and 0.5 ml of acetic anhydride was boiled for 2 min, the acetic anhydride was distilled off in a vacuum, and the oily residue was evaporated several times with benzene and then with petroleum ether; it then crystallized. After washing on the filter with a mixture of ether and petroleum ether (1:1), 0.08 g of the diacetate of the cis-syn glycol (VI) with m.p. 65-71° was obtained; on solution in ether and subsequent addition of an equal volume of petroleum ether, the diacetate (VI) formed lustrous scales with m.p. 71.5-72.5°. Found: C, 70.37; H, 7.31%. $C_{21}H_{26}O_5$. Calculated: C, 70.45;; H, 7.31%.

The cis glycol (VIII). To 25 ml of a 0.45 M ethereal solution of lithium aluminium hydride, a solution of 0.70 g of the cis diester (VIII) [3] was added, the mixture was stirred and boiled for 1 hour, and was treated with 20 ml of ethyl acetate, and then (with ice cooling) with 25 ml of 10% sulfuric acid. The organic layer was separated, washed with water, and evaporated in a vacuum. The crystalline residue was washed on the filter with a mixture of ether and petroleum ether (1:1). A yield of 0.51 g (85%) of the cis glycol (VIII) with m.p. 130-132°, having a constant m.p. of 134-135° after two recrystallizations from ethyl acetate, was obtained. Found: C, 74.65; 74.56; H, 8.09; 8.10%. $C_{17}H_{22}O_3$. Calculated: C, 74.42; H, 8.08%.

A mixture of 0.20 g of the cis glycol (VIII) and 3 ml of acetyl chloride was boiled for 30 min., the acetyl chloride was distilled off in a vacuum, and the residue was washed with benzene and then with petroleum ether, when it crystallized. After washing the reaction product on the filter with a mixture of ether and petroleum ether (1:1), 0.20 g of the diacetate of the cis glycol (VIII) with m.p. 81-82.5° was obtained; on crystallization from the same mixtures of solvents, it was obtained in the form of short thick needles with m.p. 84-85°. Found: C, 70.20; 70.40; H, 7.32; 7.37%. $C_{21}H_{26}O_5$. Calculated: C, 70.37; H, 7.31%.

The same diacetate of the cis glycol (VIII) was formed quantitatively on boiling a mixture of 0.15 g of the cis-syn glycol (VI) and 2 ml of acetyl chloride for 15 min. The derivative obtained melted at 84-85° and gave no depression of the melting point when mixed with the known sample prepared from the pure cis glycol (VI).

Hydrogenation of the cis-syn glycol (VI). A suspension of 1.10 g of the cis-syn glycol (VI) in 40 ml of dioxane was hydrogenated in the presence of 0.2 g of 30% $Pd/SrCO_3$. The substance dissolved completely during the hydrogenation. When the absorption of hydrogen was complete (1 mole), the catalyst was filtered off, and the dioxane was distilled off in a vacuum. The oily reaction product could be crystallized only partially; 0.48 g of a crystalline substance with an extended melting point of 102-117° was isolated. After its twice-repeated recrystallization from a mixture of ethyl acetate and petroleum ether (2:1) 0.20 g of the cis-syn-cis glycol (IX) was obtained in the form of fine lustrous crystals with m.p. 120-121°. Found: C, 73.59; 73.51; H. 8.74, 8.85% $C_{17}H_{24}O_3$. Calculated: C, 73.88; H, 8.75%.

A mixture of 0.14 g of the cis-syn-cis glycol (IX) and 2 ml of acetyl chloride was boiled for 30 min and worked up by the usual method. A yield of 0.16 g of the diacetate of the cis-syn-cis glycol (IX) with m.p. 99-101° was obtained; after crystallization from a mixture of ether and petroleum ether (2:1) it melted at 102-103°. Found: C, 70.02; 70.02; H, 7.82; 7.73%. $C_{21}H_{28}O_5$. Calculated: C, 69.97; H, 7.83%.

The cis-syn-cis glycol (IX). To a mixture of 50 ml of a 0.96 M ethereal solution of lithium aluminium hydride, a solution of 5.1 g of the cis-syn-cis diester (XI) [3] in 10 ml of absolute dioxane was added with stirring at such a rate that the reaction mixture boiled gently (40 min). Stirring and boiling were continued for a further 2.5 hours, and then 100 ml of ethyl acetate and 50 ml of 10% sulfuric acid were added. The crystals which separated were filtered off (1.82 g, m.p. 98-114°), and the organic layer was washed with water to a neutral reaction to Congo red, and evaporated to dryness in a vacuum. A further 1.86 g of material with m.p. 114-116° was obtained. The two portions of crystals were combined, and, after crystallization from a mixture of ethyl acetate and petroleum ether (3:2), 3.30 g of the cis-syn-cis glycol (IX) with m.p. 120-121°, which gave no depression of the melting point with a sample obtained from the hydrogenation of the cis-syn glycol (VI), was obtained.

*All melting points are corrected.

Hydrogenation of the cis glycol (VIII). A solution of 2.6 g of the cis glycol (VIII) in 50 ml of ethyl alcohol was hydrogenated in the presence of 0.5 g of 30% $Pd/SrCO_3$. One mole of hydrogen was absorbed, after which the catalyst was filtered off and the solvent was removed in a vacuum. The oily residue was dissolved in a minimum amount of methanol, ether was added, and the solution was allowed to stand overnight at 0°. In this way, 1.44 g of a crystalline substance with m.p. 99-104° was obtained, by fractional crystallization of which from a mixture of chloroform and ether, methanol and ether, and ethyl acetate and petroleum ether, we succeeded in isolating 0.22 g of the pure cis-anti-cis glycol (X) in the form of needles with m.p. 127-128°. Found: C, 73.95; 74.00; H, 8.56; 8.68%. $C_{17}H_{24}O_3$. Calculated: C, 73.88; H, 8.75%.

Boiling a mixture of 0.11 g of the cis-anti-cis glycol (X) and 2 ml of acetyl chloride for 30 min. gave the corresponding diacetate with m.p. 84-85° after the usual working up and crystallization from a mixture of ether and petroleum ether (1:2). Found: C, 69.84; 69.96; H, 7.68; 7.73%. $C_{21}H_{28}O_5$. Calculated: C, 69.97; H, 7.83%.

The cis-anti-cis glycol (X). To 10 ml of a 1 M ethereal solution of lithium aluminium hydride, a solution of 0.76 g of the cis-anti-cis diester (XII) [5] in 20 ml of absolute ether was added with stirring during 10 minutes, the mixture was boiled for 1 hour and then treated with ethyl acetate and sulfuric acid. The ethereal layer was separated, 20 ml of water was added to it, and the ether was removed in vacuum at room temperature. The crystalline reaction product was filtered off and washed with water; 0.63 g of the cis-anti-cis glycol (X) (quantitative yield) was obtained, with m.p. 111-118°. After crystallization from a mixture of ethyl acetate and petroleum ether (2:1), 0.52 g of the glycol (X) with m.p. 126-127°, not giving any depression of the melting point with a sample obtained by the hydrogenation of the cis glycol (VIII) was obtained.

SUMMARY

1. The 7-methoxy-1,2-bis-(hydroxymethyl)-hydrophenanthrenes (VI), (VIII), (IX), and (X) have been synthesized by the lithium aluminium hydride reduction of the dimethyl esters of cis-cis-Δ^4- and cis-$\Delta^{4a(10a)}$-7-methoxyhexahydrophenanthrene-1,2-dicarboxylic acids (V) and (VII) and the dimethyl esters of cis-syn-cis- and cis-anti-cis-7-methoxyoctahydrophenanthrene-1,2-dicarboxylic acids (XI) and (XIII).

2. The hydrogenation of the 7-methoxy-1,2-bis-(hydroxymethyl)-hexahydrophenanthrenes (VI) and (VIII) over 30% $Pd/SrCO_3$ takes place spatially non-selectively and leads to a mixture of the two possible geometrical isomers of 7-methoxy-1,2-bis-(hydroxymethyl)-octahydrophenanthrene.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

COMMUNICATION 10. THE DIFFERENCE IN CHEMICAL BEHAVIOR BETWEEN ALIPHATIC AND CYCLIC β-DICARBONYL COMPOUNDS

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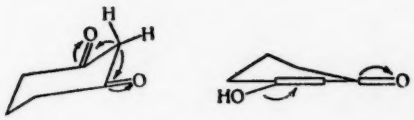
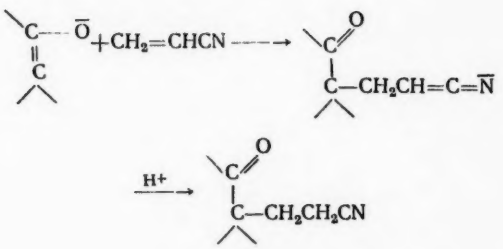
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1640-1645, September, 1961
Original article submitted February 1, 1961

A mass of experimental data show that cyclohexane-1,3-diones differ considerably in their chemical behavior from their aliphatic analogs. This difference is apparently connected with the presence of a relatively rigid cyclic system in dihydroresorcinol which creates favorable conditions for the conjugation of the single and double bonds [1].



Thanks to these structural features, cyclic β-diketones of the type of dihydroresorcinol possess an increased acidity, a high capacity for enolization, and a weakly nucleophilic center on the second carbon atom. In contrast, cyclic β-dicarbonyl compounds containing one of the keto groups outside the ring system, and aliphatic ketoenols are characterized in many cases by a weak capacity for enolization, a reduced acidity, and a high nucleophilic character. An inverse relationship is observed between the capacity of β-dicarbonyl compounds for undergoing the Michael reaction, on the one hand, and their C-acidity and enolizability, on the other hand [2], which is clearly seen, for example, when the experiments on cyanoethylation which we carried out in aqueous dioxane at 20° in the presence of 1/6 equivalent of caustic potash are considered (Table 1).

In the absence of an appreciable influence of other factors (steric hindrance, solvation) the above relationship must be manifested to the extent to which the connection of the C-acidity and the enolizability with the nucleophilic character of the α-carbon atom and with the tendency of the enolate to ketonization with displacement of the reaction center is maintained.



The strongly enolized and acidic β-dicarbonyl compounds (dihydroresorcinol, tetrinic acid) readily give stable little-reactive enolates, while the sparingly enolized weakly acidic compounds of the type of malonic and acetoacetic esters from unstable reactive enolates with a large consumption of energy. Where the parallelism between the enolizability and the C-acidity is disturbed (for example, in the case of the cyclopentanonecarboxylic and

Compound	Content of the enol in aqueous solution [3], %	Ionization constant [3]	Ionization constant		Yield of products of cyanoethylation, %					Literature references to the products of cyanoethylation
			Ketone form	Enol form	1 min	5 min	15 min	45 min	3 hr	6 hr	
α-Ethylacetoacetic ester	0,02	$1,8 \cdot 10^{-13}$	$1,8 \cdot 10^{-13}$	$2,0 \cdot 10^{-10}$	28	47	54	72	—	—	[4]
Cyclopentanone-2-carboxylic ester	0,02	$2,1 \cdot 10^{-11}$	$2,1 \cdot 10^{-11}$	$1,0 \cdot 10^{-8}$	15	22	62	79	—	—	[5]
Cyclohexanone-2-carboxylic ester	4,6	$1,4 \cdot 10^{-13}$	$1,4 \cdot 10^{-13}$	$3,2 \cdot 10^{-13}$	5	12	50	71	—	—	[5]
2-Methylindane-1,3-dione	1	$7,1 \cdot 10^{-7}$	$7,2 \cdot 10^{-7}$	$6,5 \cdot 10^{-5}$	0	0	2	17	26	31	[5]
Dimedone	95,3	$5,6 \cdot 10^{-6}$	$1,2 \cdot 10^{-4}$	$6,0 \cdot 10^{-6}$	0	0	0	0	0	0	
Dihydroresorcinol	100	$0,55 \cdot 10^{-5}$	—	$0,55 \cdot 10^{-5}$	0	0	0	0	0	0	
Tetrinic acid	100	$8,2 \cdot 10^{-5}$	—	$8,2 \cdot 10^{-5}$							

cyclohexanonecarboxylic esters) a competing influence of the factors mentioned on the capacity of the ketoenols for undergoing the Michael reaction must exist. The known [6] cases of the reduced capability of weakly acidic and weakly enolized carbonyl compounds for undergoing the Michael reaction in an aqueous medium is obviously explained by the low concentration of reacting enolates. The difference between aliphatic and cyclic β-dicarbonyl compounds is also shown in the alkylation reaction. For example, malonic and acetoacetic esters smoothly form C-alkyl derivatives with extremely diverse alkyl halides, while dihydroresorcinol alkylates satisfactorily only with allyl bromides, bromoacetic ester, and other compounds containing a labile halogen atom [7].

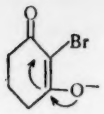
The behavior of cyclic β-dicarbonyl compounds in crotonic condensation is extremely peculiar. While with acetoacetic ester and acetylacetone, both mono- and bis-derivatives can be readily obtained, according to the ratio of the reactants, in the case of dihydroresorcinol and dimedone, even when an excess of the aldehyde is used, only the bis-derivatives can normally be obtained [8].

(I)

In consequence of their high acidity, the cyclic β-diketones may react with aldehydes without any catalyst at all [9], although the corresponding enolates, as noted above, possess a reduced nucleophilic character. The exclusive or predominating formation of the methylene-bis-cyclohexane-1,3-diones is probably explained by the high electrophilic character of the double bond of the intermediate methylene derivatives (I), the Michael reaction of which with the initial diketones takes place at a greater rate than the initial crotonic condensation. The reaction of dihydroresorcinol and dimedone with formaldehyde and amines proceeds in a similar manner, methylene-bis-diketones being obtained instead of Mannich bases (II) [10, 11]. The intermediate products in this case may be either the Mannich bases themselves, or methylene derivatives of type (I), which undergo the Michael condensation in accordance with the scheme given above.

(II)

In contrast to the corresponding aliphatic analogs [12], the enolizable 2-bromodihydroresorcinols do not enter into the reaction of nucleophilic substitution [13], obviously because of the displacement of electrons from a hydroxyl and a methylene group to the enol double bond and an increased negative charge on the second carbon atom.

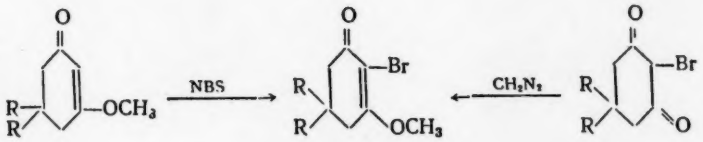


The enol ethers of aliphatic and cyclic β-dicarbonyl compounds behave completely differently with N-bromosuccinimide in carbon tetrachloride. In the case of a β-methoxycrotonic ester (III), and the cis and trans isomers of 4-methoxypent-3-one-2-one (IV), allyl bromination takes place and the corresponding β-methoxyl-γ-bromocrotonic ester (V) [14] and 4-methoxy-5-bromopent-3-en-2-one (VI) are formed.

$$\underset{\text{(III)}}{ROOCCH{=}C(OCH_3)CH_3} \xrightarrow{NBS} \underset{\text{(V)}}{ROOCCH{=}C(OCH_3)CH_2Br}$$

$$\underset{\text{(IV)}}{CH_3COCH{=}C(OCH_3)CH_3} \xrightarrow{NBS} \underset{\text{(VI)}}{CH_3COCH{=}C(OCH_3)CH_2Br}$$

In contrast, the enol ethers of dihydroresorcinol and dimedone brominate smoothly in the second position, giving 2-bromo-3-methoxycyclohex-2-enone (VIII) [15] and 2-bromo-3-methoxy-5,5-dimethylcyclohex-2-enone (VIII)



(VII), R=H
(VIII), R=CH_3

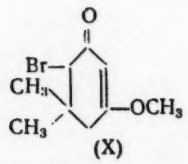
For identification purposes, we prepared 2-bromo-3-methoxy-5,5-dimethylcyclohex-2-enone by a independent route – the action of diazomethane on 2-bromodimedone.

3-Bromo-4-methoxypent-3-ene-2-one (IX), obtained by methylating 3-bromoacetylacetone with diazomethane, differs considerably in its infrared spectrum from the product of the reaction of the enol ether of acetylacetone with N-bromosuccinimide (Table 2).

$$CH_3COCHBrCOCH_3 \xrightarrow{CH_2N_2} \underset{\text{(IX)}}{CH_3COCBr{=}C(OCH_3)CH_3}$$

As was to be expected, on passing from the enol ether of acetylacetone to 4-methoxy-5-bromopent-3-ene-2-one (VI) the frequency of the CO group remains unchanged and the frequency of the double bond rises somewhat.

It is interesting to note that bromination of the enol ether of dimedone using N-bromosuccinimide has also been studied by Arakawa [16] who, carrying out the reaction in boiling carbon tetrachloride with ultraviolet irradiation, obtained 3-methoxy-5,5-dimethyl-6-bromocyclohex-2-enone (X) and a dibromide of undetermined structure, $C_9H_{12}O_2Br_2$ with m.p. 129-130°.



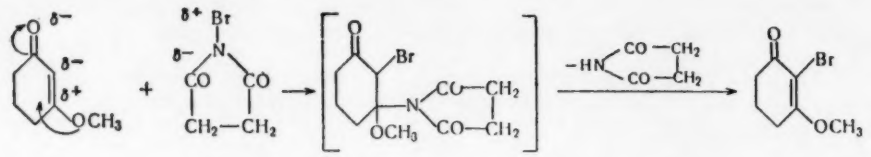
(X)

TABLE 2

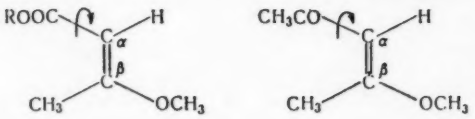
Compound	CO frequency, cm^{-1}	C=C frequency, cm^{-1}
trans-$CH_3COCH{=}C(OCH_3)CH_3$	1688	1593
$CH_3COCH{=}C(OCH_3)CH_2Br$	1688	1598
$CH_3COCBr{=}C(OCH_3)CH_3$	1671	1567

On repeating the Japanese author's experiment both with an without ultraviolet irradiation we succeeded in isolating only the dibromide mentioned from the reaction mixture. It may be assumed that Arakawa's bromide (X) arises as a result of the isomerization of the bromide (VIII) initially formed; however, we found that the latter is unchanged under the influence of ultraviolet light in boiling carbon tetrachloride.

The bromination of cyclic enol ethers with N-bromosuccinimide in the second position may be explained by an ionic mechanism with the participation of the strongly nucleophilic double bond.



The different direction of the reaction of aliphatic enol ethers (III) and (IV) with N-bromosuccinimide is, in all probability, connected with the presence in these compounds of freer rotation about the single bonds, which leads to interference with π, π-conjugation and a weakening of the nucleophilic properties of the α-carbon atom.



EXPERIMENTAL PART

Cyanoethylation of β-dicarbonyl compounds (see Table 1) was carried out by the method described earlier [5] at 20° (thermostat) in the presence of 1/6 of an equivalent of caustic potash, using 30 ml of aqueous dioxane (2:5) and 0.06 mole of the reactants, taken in equimolecular amounts. The cyanoethylation products were isolated from the reaction mixture previously acidified with dilute (1:1) hydrochloric acid after predetermined intervals of time.

Reaction of the cis-enol ether of acetylacetone with N-bromosuccinimide. A mixture of 4.3 g of the cis-enol ether of acetylacetone [b.p. 84-86° (10 mm)] [17] and 6.8 g of N-bromosuccinimide in 30 ml of carbon tetrachloride was shaken at room temperature for 24 hours; then it was filtered and evaporated in a vacuum. The residue was dissolved in ether and cooled to -70°. Under these conditions, 2.9 g (38%) of 4-methoxy-5-bromopent-3-en-2-one (VI) with m.p. 50-52° separated. Found: C, 37.53; 37.30; H, 4.78; 4.65; Br, 41.01; 41.11%. $C_6H_9O_2Br$. Calculated: C, 37.32; H, 4.69; Br, 41.39%.

Under the same conditions, 3.4 g of the trans-enol ether of acetylacetone [b.p. 59-61° (10 mm)] [17] gave 3.32 g (55%) of the above-mentioned bromide (VI) with m.p. 51-53°.

O-Methylation of 3-bromoacetylacetone. A mixture of 2.3 g of 3-bromoacetylacetone (m.p. 28-29°) [1], 3 ml of methanol, and a two-fold excess of an ethereal solution of diazomethane was allowed to stand for 12 hours at room temperature. After vacuum evaporation, the residue was dissolved in ether and cooled to -70°. Under these conditions, 2.1 g (84%) of 3-bromo-4-methoxypent-3-ene-2-one (IX), with m.p. 29-30°, separated. Found: C, 37.20; 37.37; H, 4.68; 4.71; Br, 41.18; 41.06%. $C_6H_9OBr_2$. Calculated: C, 37.32; H, 4.69; Br, 41.39%. The bromide obtained gave a depression of the melting point with 4-methoxy-5-bromopent-3-ene-2-one (VI).

Bromination of dimedone. To a suspension of 1.4 g of dimedone in 20 ml of water, 1.6 g of bromine was added and the precipitate which formed was filtered off and recrystallized from water. A yield of 2.1 g (96%) of 2-bromodimedone with m.p. 173-174° was obtained. 2-Bromodimedone prepared by the bromination of dimedone in chloroform had the same melting point.

O-Methylation of 2-bromodimedone. To a suspension of 1.3 g of 2-bromodimedone in 20 ml of ether, a two-fold excess of an ethereal solution of diazomethane were added. The mixture obtained was evaporated in vacuum and the residue was recrystallized from hexane. The yield of 2-bromo-3-methoxy-5,5-dimethylcyclohex-2-enone

(VIII) was 1.2 g (89%); m.p. 104-105°. Found: C, 46.50; 46.59; H, 5.53; 5.58; Br, 34.10; 34.27%. $C_9H_{13}O_2Br$. Calculated: C, 46.35; H, 5.62; Br, 34.34%.

On shaking with dilute (1:1) hydrochloric acid in the cold (10-15 min), 2-bromo-3-methoxy-5,5-dimethylcyclohex-2-enone (VIII) was quantitatively converted into 2-bromodimedone.

Reaction of the enol ether of dimedone with N-bromosuccinimide. A mixture of 0.5 g of the enol ether of dimedone [16] and 0.59 g of N-bromosuccinimide in 10 ml of carbon tetrachloride was kept for 24 hours at 20° and was then filtered and evaporated in vacuum. After the residue has recrystallized from hexane, 0.5 g (71%) of 2-bromo-3-methoxy-5,5-dimethyl-cyclohex-2-enone (VIII) with m.p. 104-105° was obtained.

A mixture of 1.5 g of the enol ether of dimedone and 1.8 g of N-bromosuccinimide in 20 ml of carbon tetrachloride was boiled for 20 minutes while being irradiated with a mercury lamp. After filtration and evaporation of the mother liquors, 0.7 g of Arakawa's dibromide with m.p. 129-130° [16] was isolated.

The infrared spectra ($CHCl_3$) were taken by L. A. Leites, to whom the authors express their grateful thanks.

SUMMARY

Cases of the different chemical behavior of aliphatic and cyclic β-dicarbonyl compounds have been considered. The following properties are characteristic for β-diketones of the type of dihydroresorcinol: hindered Michael and C-alkylation reactions, tendency to form alkylidene-bis-β-diketones by the action of aldehydes, incapability of undergoing the Mannich reaction, inertness of the halogen atom of enolized 2-bromo derivatives, and the bromination of the enol ethers by N-bromosuccinimide in the second position.

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THE CHEMISTRY OF ACETALS

COMMUNICATION 6*. THE DIMERIZATION OF ACETALS OF α, β-UNSATURATED ALDEHYDES

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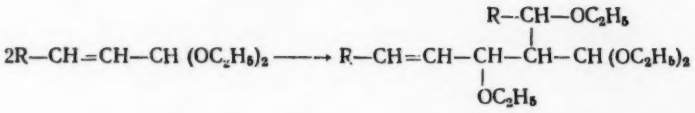
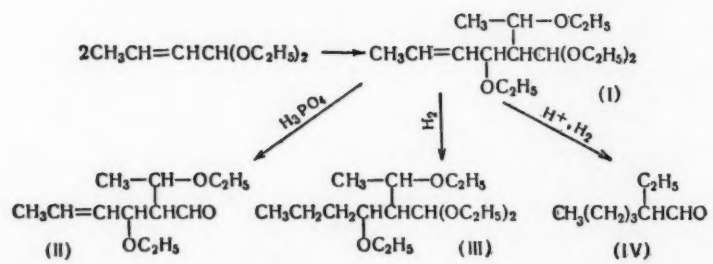
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1646-1649, September, 1961
Original article submitted February 21, 1961

The addition of acetals to an activated double carbon–carbon bond is one of the methods for lengthening a hydrocarbon chain. However, only in the case of vinyl ethers does this addition lead to reactive compounds (acetals of aldehydes) which may be used for further chemical conversions. We made an attempt to use the dimerization of acetals of α, β-unsaturated aldehydes for lengthening a hydrocarbon chain [1]; as a result of this reaction one molecule of the acetal adds to the double bond of the other with the formation of an alkoxyacetal according to the following scheme:



The dimerization was studied using the diethyl acetals of acrolein and crotonic and dimethylacrylic aldehydes as examples, and the results obtained form the subject of the present communication.

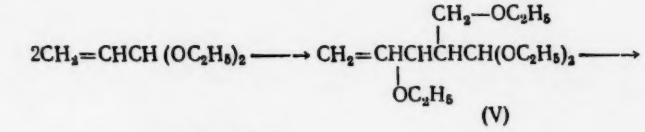
We established that the dimerization reaction proceeds most readily in the case of the acetal of crotonic aldehyde which, on the addition of boron trifluoride etherate at -40° or of an ethereal solution of zinc chloride at room temperature, gives a single dimer (I) with a yield of 80-90%. Under these conditions, the dimerization goes quite smoothly and does not require the use of a solvent. Judging from the Raman spectrum, this dimer contains a single isolated double bond (γ 1672.5 cm^{-1}), and on saponification it gives an unsaturated diethoxyaldehyde [2], which was characterized in the form of it semicarbazone. On hydrogenation with a Pd catalyst, the dimer (I) absorbed one mole of hydrogen and was converted into the saturated diethoxyaldehyde (III). Exhaustive hydrogenolysis of the dimer, with subsequent saponification, gives 2-ethylhexanal (IV), the 2,4-dinitrophenylhydrazone of which proved to be identical with an authentic sample. All these results show that the initial dimer (I) has the structure 2-(1'-ethoxyethyl)-ethoxyhex-4-enal and its formation takes place as a result of addition according to the scheme discussed above.



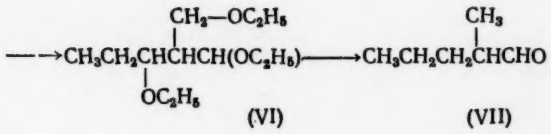
*Communication 5, see [2].

The formation of the dimer of the acetal of acrolein proceeds in an analogous manner. However, the dimer (V) is obtained with a yield of only ~10% in this case, the reaction having to be carried out in ether at -30°. Under these conditions, the main product is the trimer, the conversions and a proof of the structure of which have been reported earlier [2]. On hydrogenating the dimer (V), one mole of hydrogen is absorbed and the saturated diethoxyacetal (VI) is formed, which is characterized in the form of its 2,4-dinitrophenylhydrazone. By analysis, the dimer (V) has four alkoxy groups, and on saponification gives a mixture which, according to the infrared spectrum, contains ~30% of α,β-unsaturated aldehyde.

On hydrogenolysis of the dimer (V), we succeeded in isolating an aldehyde, the 2,4-dinitrophenylhydrazone of which gave no depression of the melting point when mixed with the hydrazone of 2-methylvaleraldehyde (VII) and, consequently, the initial dimer (V) is the diethylacetal of 2-(ethoxymethyl)-3-ethoxypent-2-enal.

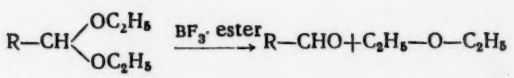


(V)

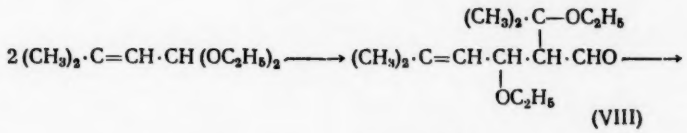


(VI) (VII)

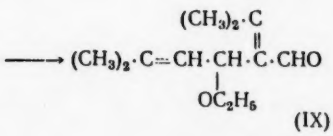
We carried out the dimerization of the acetal of dimethylacrylic aldehyde using boron trifluoride etherate without a solvent at -20°. In spite of the fact that this reaction was carried out under conditions excluding the entry of moisture, the single substance formed in this process with a yield of 30% is not an acetal and, by analysis, corresponds to the product of the condensation of a molecule of dimethylacrylic aldehyde with its acetal (VIII). We have noted that when any acetals are treated with boron trifluoride etherate their partial saponification always takes place, though this is not the usual hydrolysis reaction but proceeds according to the scheme:



Apparently, in the case of the acetal of dimethacrylic aldehyde this reaction goes at a great rate. The dimer (VIII), even on distillation, partially eliminates one ethoxy group giving the α, β-unsaturated aldehyde (IX) with λ_{max} 238.5 mμ (alcohol). This is possible only if the ethoxy group splits out from a tertiary carbon atom. On the basis of these results, we consider that the dimerization of the acetal of dimethylacrylic aldehyde takes place in accordance with the general scheme described above and the dimer formed (VIII) has the structure of the diethylacetal of 2-(1'-ethoxy-1'-methylethyl)-3-ethoxy-5-methylhex-4-enal:



(VIII)



(IX)

The material illustrated above shows that a double bond conjugated with an acetal or carbonyl group is sufficiently active to add acetals of unsaturated aldehydes and, under some conditions, this reaction may be used to lengthen a hydrocarbon chain.

EXPERIMENTAL PART

Dimerization of the diethyl acetal of crotonic aldehyde. To 14.4 g (0.1 mole) of the acetal at a temperature of -40°, 1 ml of BF_3 etherate was added dropwise, and the mixture was stirred for 45 minutes, and neutralized with solid sodium bicarbonate. The mixture was diluted with ether and filtered. Distillation yielded 12.1 g (84 %) of the dimer (I) with b.p. 86-88° (1.5 mm); n_D^{20} 1.4328. After distillation through a column, the dimer had b.p. 83-84° (2mm); n_D^{21} 1.4324. Found: C, 66.61; 66.65;; H, 11.03; 10.92%; mol.wt., mean, 281. $C_{16}H_{32}O_4$. Calculated; C, 66.63; H, 11.18%; mol.wt. 288. The Raman spectrum showed the presence of an isolated double bond, ν 1672.5 cm^{-1}.

The same reaction goes well with a saturated solution of $ZnCl_2$ in ether (5 ml to 0.1 mole of acetal). In this case, the mixture must be maintained at room temperature for 3 hours.

Saponification of the dimer (I). A mixture of 7 g of the dimer (I) and 4.5 ml of 10% H_3PO_4 was heated in a current of nitrogen for 8 hours at 90°. The reaction product was washed with bicarbonate solution and extracted with ether. After drying over $MgSO_4$ and distillation, 4.2g (77%) of the diethoxyaldehyde (II) with b.p. 66-69° (1 mm); n_D^{21} 1.4428, which contained ~3% of the α,β-unsaturated aldehyde, was obtained. Infrared spectrum: ν 1638, 1675, 1723 cm^{-1}; λ_{max} 271 mμ (alcohol). Found: C, 67.17; 67.16; H, 10.10; 10.12%. $C_{12}H_{22}O_3$. Calculated: C, 67.25; H, 10.35%.

Semicarbazone. Found: C, 57.54; 57.58; H, 9.17; 9.29; N, 15.56; 15.54%. $C_{13}H_{25}O_3N_3$. Calculated: C, 57.54; H, 9.29; N, 15.49%.

Hydrogenation of the dimer (I). A solution of 10.1 g of the dimer (I) in alcohol was hydrogenated with a Pd catalyst on $SrCO_3$, 1 mole of hydrogen (880 ml) being absorbed. After distillation, 7.5 g of a substance with a pleasant floral smell was obtained: b.p. 90-91° (2 mm); n_D^{27} 1.4222, which, from analysis, corresponds to the saturated diethoxyacetal (III). Found: C, 66.14; 66.10; H, 11.70; 11.86%. $C_{16}H_{34}O_4$. Calculated: C, 66.16; H, 11.80%.

Hydrogenolysis of the dimer (I). A solution of 5.9 g of the dimer (I) in 30 ml of acetic acid was hydrogenated with a mixture of 0.5 g of 20% Pt/C and 0.3 g of $PdCl_2$. After the absorption of 3 moles of hydrogen, the catalyst was filtered off and the mixture was diluted with water to accelerate the saponification of the acetal. After neutralization, extraction with ether, and drying with $MgSO_4$, 0.7 g (27%) of 2-ethylhexanan (IV) with b.p. 70-71° (26 mm); n_D^{23} 1.4186 was obtained. Its 2,4-dinitrophenylhydrazone had m.p. 122-123°, λ_{max} 338 mμ (alcohol) and gave no depression of the melting point in admixture with a known sample of the 2,4-dinitrophenylhydrazone of 2-ethylhexanal. Found: C, 54.10; 54.25; H, 6.63; 6.67; N, 18.52; 18.57%. $C_{14}H_{20}O_4N_4$. Calculated: C, 54.53; H, 6.54; N, 18.17%.

Production of the dimer of the acetal of acrolein. To a solution of 56.7 g of the acetal of acrolein [3] in 150 ml of absolute ether, cooled to −40°, 11 ml of boron trifluoride etherate was added during 25 min in such a way that the temperature did not rise above −35°. The reaction mixture was maintained at this temperature for 1 hour and then an excess of solid sodium bicarbonate was added, the mixture was stirred at room temperature for some hours and left overnight. The residue of salt was filtered off and washed with ether, and the reaction product was distilled in a vacuum: fraction I: 5.5 g, b.p. 81-89° (2 mm); n_D^{20} 1.4296; fraction II: 34.2 g, b.p. 148-158° (2 mm); n_D^{20} 1,4450; fraction III: 6.6 g, b.p. 166-190° (2 mm); n_D^{20} 1.4488.

After redistillation of fraction I, 4.1 g (~7%) of the dimer (V) was obtained with b.p. 105-108° (7 mm), n_D^{20} 1.4284. Found: C, 64.27; 64.23; H, 10.70; 10.49%; mol·wt [4], mean, 261. $C_{14}H_{28}O_4$. Calculated:C, 64.58; H, 10.84%; mol·wt 262.4.

Fraction II consisted mainly of the trimer, the structure of which has been described earlier [2].

Hydrogenation of the dimer (V). A solution of 5.8 g of the dimer (V) in 10 ml of ethyl alcohol was hydrogenated over Pt/asbestos. It absorbed 510 ml of hydrogen (1 mole) in 40 min. After distillation, 4.6 g of the saturated diethoxyacetal (VI) was obtained, with b.p. 103-105° (7 mm); n_D^{20} 1.4226. Found: C, 64.16; 64.04; H, 11.49; 11.43%. $C_{14}H_{30}O_4$. Calculated C, 64.08; H, 11.53%.

The 2,4-dinitrophenylhydrazone obtained from it formed yellow needles with m.p. 94-95° (alcohol+ petroleum ether); λ_{max} 340 mμ (isooctane). Found: C, 52.50; 52,32; H, 6.45; 6.59; N, 15.18; 15.07; C_2H_5O, 23.36; 23.30%. $C_{16}H_{24}O_6N_4$. Calculated: C, 52.16; H, 6.55; N, 15.21; C_2H_5O, 24.9%.

Saponification of the dimer (V). A mixture of 2 g of the dimer (V) and 10 ml of 10% phosphoric acid was heated for 1 hour at 70°. The reaction mixture was neutralized with sodium bicarbonate solution and extracted with ether, and the extract was dried with magnesium sulfate. After distillation, 0.6 g of an aldehyde with b.p. 114-117° (30 mm); n_D^{20} 1.4296 was obtained. Its infrared spectrum had characteristic absorption bands at ν, 1694 cm^{-1}; k, 164.2; ν, 1726 cm^{-1}; k, 402, which indicates the presence in it of ~30% of the α,β-unsaturated aldehyde and ~70% of the saturated aldehyde (VI).

Hydrogenolysis of the dimer (V). On hydrogenolysis of the dimer (V) as described for the dimer (I), a mixture of aldehydes was obtained. A 2,4-dintrophenylhydrazone with m.p. 108-111° (alcohol) was obtained from them: λ_{max} 361 mμ. Found: C, 51.33; 51.34; H, 5.60; 5.79. N, 20.15; 20.06%. $C_{12}H_{16}O_4N_4$. Calculated: C, 51.42; H, 5.75; N, 19.99%. This hydrazone gave no depression of the melting point with the 2,4-dinitrophenylhydrazone of 2-methylpentanal.

Dimerization of the acetal of dimethacrylic aldehyde. Ten grams of the acetal of dimethacrylic aldehyde [5] was introduced into a carefully dried flask in a current of dry nitrogen and cooled to −20°, 1 ml of BF_3 etherate was added, and the mixture was stirred at this temperature for 6 hours. The reaction mixture was neutralized with sodium bicarbonate, diluted with ether, warmed to room temperature, and left overnight. After separating off the residue and distillation, there was obtained 3.8 g of a mixture of dimethacrylic aldehyde and its acetal with n_D^{20} 1.4244 (initial acetal, n_D^{20} 1.4208); 2.3 g (30%) of the dimer (VIII) with b.p. 94-99° (1.5 mm); n_D^{20} 1.4528; λ_{max} 238.5 mμ (alcohol); ε 7650; and 1.4 g of residue. After redistillation, the constants of the dimer (VIII) obtained did not fundamentally change. Found: C, 69.53; 69.62; H, 10.19; 10.35%. $C_{14}H_{26}O_3$. Calculated: C, 69.38; H, 10.81%.

SUMMARY

The dimerization of the acetals of acrolein and crotonic and dimethylacrylic aldehydes under the influence of boron trifluoride has been sutdied and the structure of the dimers obtained has been demonstrated.

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CHEMISTRY OF ACETALS

7. POLAROGRAPHIC INVESTIGATION OF SOME HYDROLYSIS PRODUCTS OF TETRAETHYL ACETALS OF MALONIC AND β-ETHOXYGLUTARIC DIALDEHYDES

L. A. Yanovskaya and V. F. Kucherov

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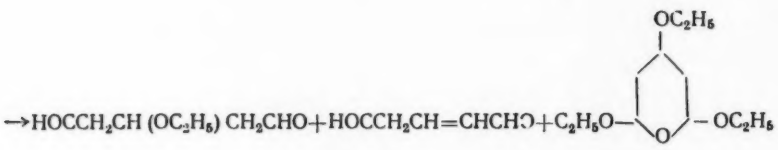
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1650-1657, September, 1961
Original article submitted February 21, 1961

As described earlier [1-3] hydrolysis of the tetraethyl acetals of malonic and β-ethoxyglutaric dialdehydes as a function of the amount of water used can occur by different possible routes and can lead to formation not only of dialdehydes but also of other conversion products. Thus, in the presence of excess water hydrolysis can occur according to the schemes:

$$(C_2H_5O)_2CHCH_2CH(OC_2H_5)_2 \rightarrow HOCCH_2CHO$$
$$(C_2H_5O)_2CHCH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \rightarrow \quad (1)$$

(2)

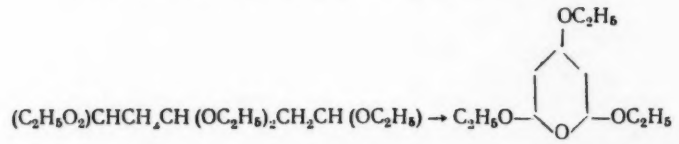


$$\rightarrow HOCCH_2CH(OC_2H_5)CH_2CHO + HOCCH_2CH{=}CHCHO + C_2H_5O-\text{(O-ring)}-OC_2H_5$$

In the presence of just an equivalent amount of water the hydrolysis goes according to the schemes:

$$(C_2H_5O)_2CHCH_2CH(OC_2H_5)_2 \rightarrow C_2H_5OCH{=}CHCHO \quad (3)$$

(4)



$$(C_2H_5O_2)CHCH_4CH(OC_2H_5)_2CH_2CH(OC_2H_5) \rightarrow C_2H_5O-\text{(O-ring)}-OC_2H_5$$

With developing a method for determining the hydrolysis products and controlling these processes as a function of reaction conditions (time, temperature) as goals, as well as clarifying the influence of the ethoxy group in the β-position relative to the carbonyl group in β-unsaturated aldehydes, we studied the polarographic behavior of some β-ethoxyacroleins of the type $C_2H_5OCH{=}C(R)CHO$ (R = H, CH_3, N = C_5H_{11}), obtained by scheme 3, as well as the sodium salts of enolic malonic dialdehyde, bromomalonic and malonic dialdehydes obtained by scheme 1. Besides that, polarographic studies were carried out on the sodium salt and enol benzoate of glutaconic dialdehyde obtained after a similar work up [3] of the reaction mixture from the hydrolysis products in scheme 2.

EXPERIMENTAL

The polarogram plot was obtained on an electronic self-recording polarograph TsLA meter. The dropping electrode was provided with a blade for forced breaking of the drop and had the characteristic m = 1.628 mg/sec, t = 0.29 sec . The height of the mercury column (H) during measurements was equal to 45 cm. The cell was thermostated at a temperature of 25°. The backgrounds used were 0.1 N HCl, 0.1 N KCl, 0.1 N NaOH or KOH and buffer mixtures [4] of composition 0.2 N HCl - 0.2 N KCl (pH 1-2.2), 0.2 M K_2HPO_4 -0.1M citric acid (pH-2.2-8), 0.1 N borax-0.1 N HCl (or 0.1 N NaOH) (pH-7.94-12.37). The pH value was monitored by an LP-5 potentiometer. All solutions were swept with nitrogen during polarography to expel oxygen.

β-Ethoxyacrolein 2(I)*, β-ethoxy-α-methacrolein (II), β-ethoxy-α-n-amylacrolein (III), the sodium salt of enolic malonic dialdehyde (IV), the sodium salt of enolic glutaconic dialdehyde (V), and the enol benzoate of glutaconic dialdehyde (VI) were prepared by previously described methods [1,3].

TABLE 1

Substance	First wave				First wave			
	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$
(I)	1,1	—1,100	1,48	32,2	4,10	—1,325	0,57	60
(II)	1,1	—1,190	1,89	60	4,10	—1,35	0,10	75
(IV)	1,1	—1,132	0,94	88	4,10	Not taken		
(I)	2,12	—1,225	1,09	73	5,15	Wave poorly defined		
(II)	2,12	—1,280	1,36	—	5,15	—1,410	0,735	115
(IV)	2,12	—1,212	0,91	88	5,15	No wave		
(I)	3,12	—1,250	0,90	80	6	—1,38	0,19	—
(II)	3,12	—1,310	0,90	—	6	—1,42	0,12	—
(III)	3,12	—1,020	0,94	70	7	—1,232	0,35	116
(IV)	3,12	—1,248	0,63	82	6	No wave		

Substance	Second wave				Second wave			
	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$
	5,15	—1,698	1,73	148	9,24	—1,700	0,17	—
(I)	6	—1,687	2,05	164				
(II)	4,1	—1,550	0,03	67	9,24	—1,750	1,45	100
	5,15	—1,730	0,05	110				
	6	—1,760	0,53	98				
(III)	6	Not taken			9,24	—1,825	0,71	112
(IV)	6	—1,757	0,92	137	9,24	No wave		
(I)	7	—1,778	2,26	178	11,07	—1,70	1,45	—
(II)	7	—1,760	1,82	98	10,97	—1,730	1,72	92
(I)	8	—1,695	—	95	12,37	—1,70	0,09	—
(II)	8	—1,725	1,51	75				

As was expected, 2,4,6-triethoxytetrahydropyran, obtained by route (4), was polarographically inactive. As can be seen from the data presented in Table 1, compounds (I)-(IV) generate two waves. The first wave occurs in acidic medium close to pH 6-7, but in the case of (IV) this wave disappears at pH 5.15. The half-wave potential of the first wave is shifted in the direction of greater negative potentials by increasing the pH of the medium. Wave height falls markedly on transition to a less acidic range. Within the limits pH 1-4, there is a linear relation between the value of the limiting current and $\sqrt{H}$. Thus, the first wave has diffusion character. In the limits of concentration studied (1-3 mM/l) through pH 1-4 a linear dependency is maintained between wave height and concentration of β-ethoxyacrolein, which permits defining the first-wave height for these substances under these conditions.

The second wave occurs at pH 5-6 and remains to pH 12, with the exception of (IV) for which the second wave is not observed until about pH 9.24. The half-wave potential of the second wave is nearly independent of the pH of the medium. The second-wave height also rapidly diminishes with increasing pH of the medium. Like the first wave, the second-wave possesses diffusion character (linear dependence is observed between the value of limiting current and $\sqrt{H}$). Linear dependency is observed between the second-wave height and concentration particularly at pH 7-9. Typical polarograms of substances (I), (II), and (IV) are presented on Figs. 1-3.

If the data we obtained for (I), (II), (III), and (IV) are compared with the literature data for acrolein [5-8] and crotonaldehyde [6,8, and 9], then the conclusion can be drawn that these compounds are reduced by similar processes at a dropping mercury electrode. However, a series of peculiarities are observed. To begin with, the half-wave potentials for the first waves of all the compounds we studied in acidic media are much more negative than of acrolein or crotonaldehyde (Table 2). Furthermore, the first-wave height of (I), (II), and (III) rapidly decreases with increasing pH and disappears at pH 6, while the wave for acrolein and crotonaldehyde remains up to near pH 12 and its height does not depend on pH.

* Purity of product 75%.

Thus, in acidic media β-ethoxyacroleins are characterized by more difficult reduction than acrolein or crotonaldehyde. The rapid fall of wave height with increasing pH of the medium points out some modification of the β-ethoxyacrolein molecule which lessens its polarographic activity function; it is known that the first-wave reduction of α,β-unsaturated aldehydes is related to reduction of the double bond.

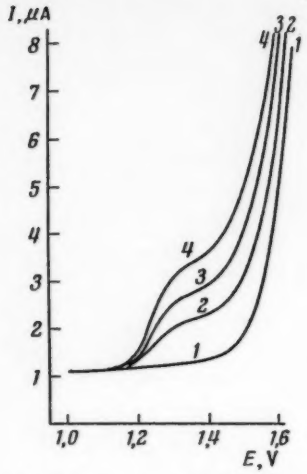


Fig. 1. Polarogram of β-ethoxyacrolein (I) at pH 3.12; 1) background; 2) c = 0.935 mM/l; 3) c = 1.71 mM/l; 4) c = 2.738 mM/l.

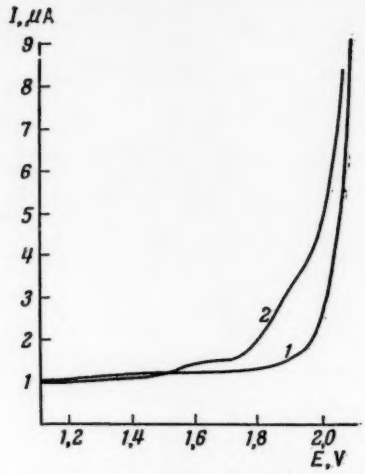


Fig. 2. Polarogram of β-ethoxy-α-methacrolein (II) at pH 6.21; 1) background; 2) c = 0.805 mM/l.

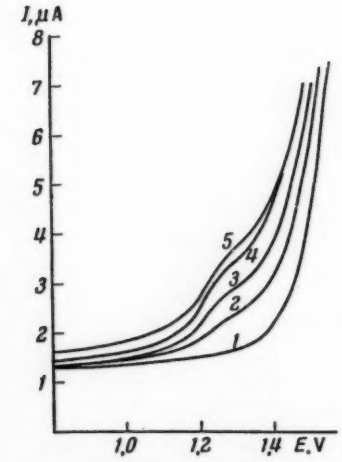


Fig. 3. Polarogram of the sodium salt of enolic malonic dialdehyde at pH 2.69; 1) background; 2) c = 0.825 mM/l; 3) c = 1.50 mM/l; 4) c = 1.50 mM/l, H = 90 cm; 5) c = 2.10 mM/l.

It should be noted that the first-wave height at pH 1-6 is practically unchanged over a period of 6-7 hr, but completely disappears after 24 hr.

The second wave of (I)-(IV) approximates the half-wave potential value for the upper limiting wave of saturated aldehydes, in particular the value for the half-wave potential of β-ethoxypropionaldehyde $E_{1/2}$ = −1.688 V in the range pH 6-10) the polarographic behavior of which we studied for comparison; it was shown that it does not differ in behavior from ordinary saturated aldehydes.

However the second-wave height of β-ethoxyacrolein, in contrast to the second-wave height of acrolein and crotonaldehyde and the wave height of β-ethoxypropionaldehyde, falls sharply with increasing pH and in sodium hydroxide solutions these compounds give almost no wave. Evidently this must explain the ease of transforming the aldehyde group of β-ethoxyacroleins in alkaline medium. From the discussion it is evident that the presence of ethoxy group in the β-position of acrolein influences the polarographic behavior of the molecule in a definite manner.

We also studied the polarographic behavior of (V) and (VI). Typical polarograms of (V) and (VI) are presented in Fig. 4 and 5. The results obtained are presented in Table 3. These compounds resemble hexadien-2,4-al [9] in their behavior with the exception that the second reduction wave of (V) and (VI) occurs not only in alkaline but also in acidic media. Furthermore, in alkaline medium the sodium salt of (V) has a third wave, representing, apparently, reduction of anionic form of (V). The first and second waves of (V) and (VI) have diffusion character (linear dependency is observed between limiting current and $\sqrt{H}$). For both (V) and (VI) linear dependence is observed between the heights of the first and second waves and concentration particularly near pH 1.1. The third wave of (VI) is not cleanly a diffusion [wave]. Thus, the presence of the benzoate group in the δ-position to the aldehyde group has little influence on polarographic behavior.

Comparison and analysis of the polarographic behavior of malonic dialdehyde (Table 4) with that of β-ethoxyacrolein and the sodium enolate of (IV) allow the conclusion that malonic dialdehyde is present in solution principally in its enolic form, which fits the chemical behavior of malonic dialdehyde and the data obtained from studying the UV spectrum of this compound, which was prepared by hydrolysis of malonic dialdehyde tetramethyl acetal [10]. It is possible to arrive at a similar conclusion by comparing the behavior of bromomalonic dialdehyde with β-ethoxyacrolein, the sodium salt of (IV), and saturated α-bromoaldehydes [11] (see Table 4). This outcome is also supported by chemical data [12] and the results of UV spectral study of bromomalonic dialdehyde, which displays a maximum characteristic of α,β-unsaturated ketones at high absorption intensity (λ_{max} 274 mμ, ε = 19,000) in alcoholic solution.

TABLE 2

Substance	Medium	(pH)$E_{1/2}$, V relative units	Literature citation
Acrolein	0.09	NHCl−0.85	[6]
Crotonaldehyde	0.09	NHCl−0.9	[6]
	Acetate buffer	(1.3) −0.937	[9]
	" "	(3.3) −1.025	[9]
	" "	(5.3) −1.150	[9]
(I)	0.1	NHCl−1.35	Our data
	Buffer solution	(1.1) −1.10	" "
	" "	(3.12)−1.250	" "
	" "	(5.15) Wave poorly defined	" "
(II)	0.1	NHCl−1.37	Our data
	Buffer solution	(1.1) −1.190	" "
	" "	(3.12)−1.310	" "
	" "	(5.15)−1.410	" "

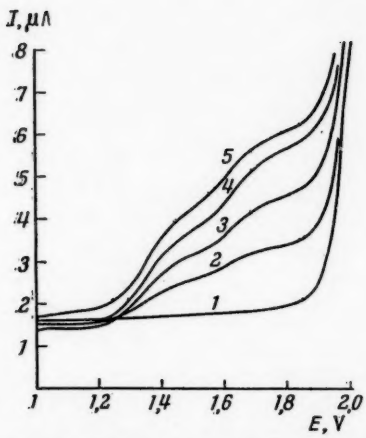


Fig. 4. Polarogram for enol benzoate of glutaconic dialdehyde (VI) at pH 1.1; 1) background; 2) c = 0.188 mM/l; 3) c = 0.188 mM/l, H = 90 cm; 4) c = 0.383 mM/l; 5) c = 0.530 mM/l.

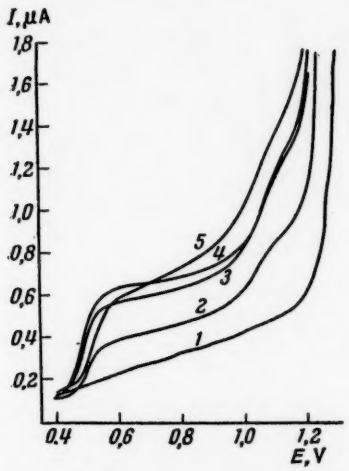


Fig. 5. Polarogram for sodium enolate of glutaconic dialdehyde (V) at pH 7; 1) background; 2) c = 1.84 mM/l; 3) c = 3.39 mM/l; 4) c = 4.69 mM/l; 5) c = 3.39 mM/l, H = 90 cm.

TABLE 3

Substance	First wave				Second wave				Third wave			
	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inn-i}}{\Delta E}$	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{\quad}}{\quad}$
(V)	1,1	—0,775	4,15	122	1,1	—1,123	0,25	108				
(VI)	1,1	—0,510	0,94	231	1,1	—1,07	1,25	73				
(V)	2,12	—0,845	2,60	87	2,12	—1,260	0,42	105				
(VI)	2,12	—0,540	1,10	39	2,12	—1,143	1,41	57				
(V)	3	—0,738	2,26	100	3	—1,208	4,15	115				
(VI)	3	—0,630	0,99	35	3	—1,175	1,85	68				
(V)	4	—1,01	1,88	105	4	—1,430	2,60	135				
(VI)	4	—0,803	0,99	40	4	—1,177	0,78	47				
(V)	5	—0,910	1,02	105	5	—1,230	1,75	180				
(V)	6	No wave			6	—1,270	3,58	175	6	—1,580	1,79	113
(V)	7	» »			7	—1,375	0,78	168	7	—1,663	1,26	97
(V)	8	» »			8	Very small wave			8	—1,600	3,76	190
(V)	9,24	» »			9,94	No wave			9,24	—1,710	4,25	185
(VI)	9,24	» »			9,24	—1,130	3,1	92	9,24	No wave		
(V)	9,97	» »			9,97	No wave			9,97	—1,780	3,46	102
(V)	11,07	» »			11,07	» »			11,07	—1,770	3,00	110
(V)	12,37	» »			12,37	» »			12,37	—1,780	0,58	119

We also studied the polarographic behavior of one of the dialdehydepolyenes not previously studied, namely octatrien-2,4,6-dial-1,8 [13] (Fig. 6 and Table 5). This compound has only one polaragraphic wave within the pH 1-12 limits; the half-wave potential remains constant at pH 9.24. The wave has diffusion character (linear dependence is observed between limiting current and $\sqrt{H}$).

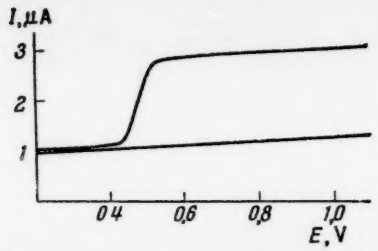


Fig. 6. Polarogram for octatrien-2,4,6-dial-1,8 at pH 7.

In conclusion we wish to thank S. G. Mairanovskii for valuable advice in the execution and discussion of this work.

SUMMARY

β-Ethoxyacrolein, β-ethoxy-α-methylacrolein, β-ethoxy-α-amylacrolein, the sodium enolate of malonic dialdehyde, bromomalonic dialdehyde, and octatrien-2,4,6-dial-1,8 were reduced at a dropping mercury electrode. The reduction waves had diffusion character.

TABLE 4

pH	$E_{\frac{1}{2}}$, V relative units				K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$
			Malonic dialdehyde			
1,1	Wave blends with background					
5,15	—1,03;	—1,43;	—1,69;	2,45	—; 75;	110
7	—1,53;	—1,79	—; —		—;	122
9,24	No wave					
			Bromomalonic dialdehyde			
2,12	—1,01;	—1,22	1,68	0,44	110;	39
3,12		—1,19		1,150		152
7		—1,36		0,82		115
9,24		—1,42		1,56		100

TABLE 5

pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$	pH	$E_{\frac{1}{2}}$, V relative units	K	$\frac{\Delta \lg \frac{i}{inp-i}}{\Delta E}$
1,1	—0,135	3,28	—	7	—0,472	2,79	44
2,12	—0,150	4,01	50	9,24	—0,620	3,14	44
3,12	—0,244	2,60	46	11,07	—0,636	3,02	44
5,15	—0,372	2,60	44	12,37	—0,630	2,65	44

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ALKENYLATION OF p- and o-CRESOLS WITH PIPERYLENE

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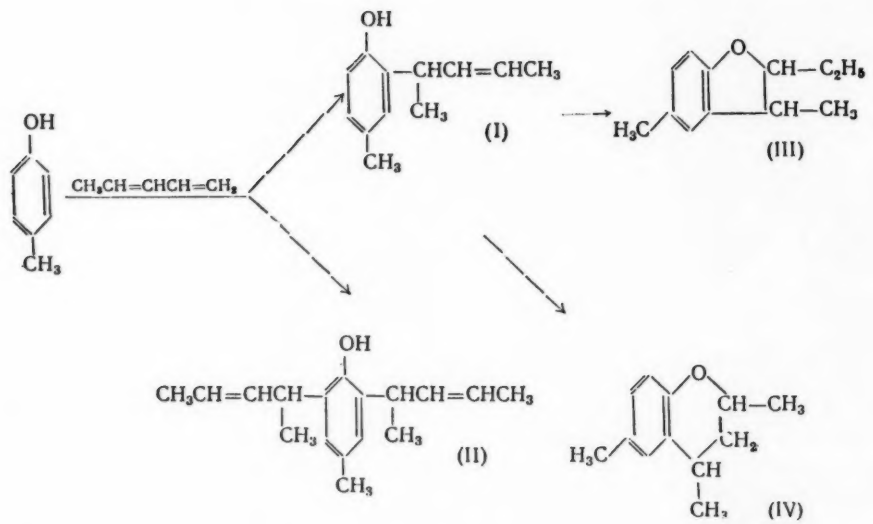
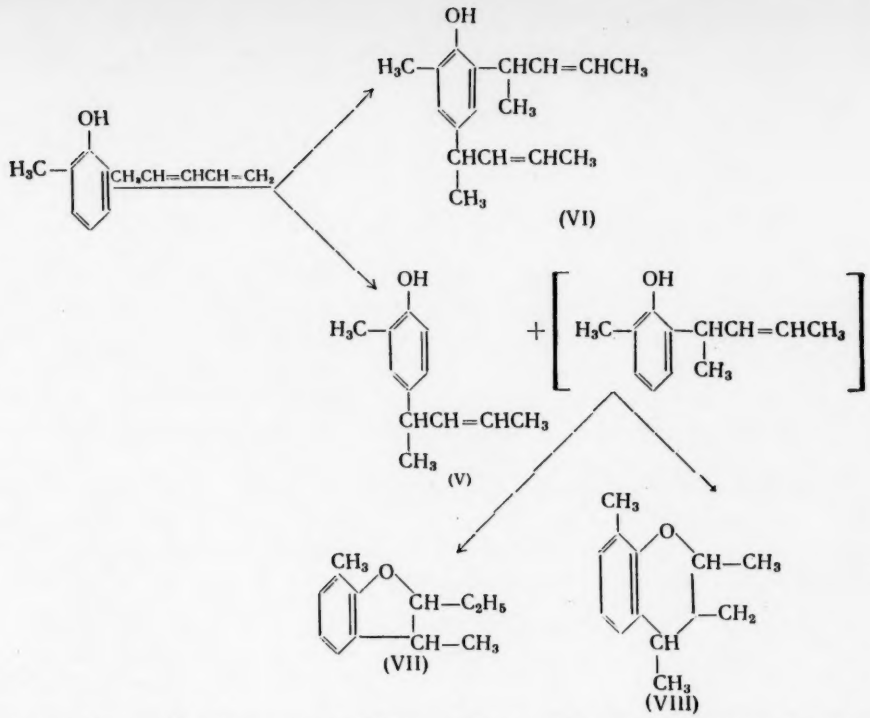
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1657-1660, September, 1961
Original article submitted February 20, 1961

Continuing our work on alkenylation of phenols with doubly unsaturated hydrocarbons [1-3] we attempted alkenylation of p- and o-cresols with piperylene in the presence of some acid catalysts—ethylsulfuric acid, zinc chloride deposited on aluminum oxide, and cationite KU-1. Alkenylation of p-cresol with piperylene in the presence of ethysulfuric acid at 50° led only to the formation of neutral reaction products—3,5-dimethyl-2-ethylcoumaran, 2,4,6-trimethylchroman, and high boiling substances the structure of which was not studied. Alkenylation products in the presence of zinc chloride on aluminum oxide at 150° were also neutral compounds (~38%). Apparently, under the conditions we selected, overall cyclization occurred forming o-pentenyl-p-cresol mixed with the corresponding chroman (IV) and coumaran (III). However, by conducting the reaction in the presence of the less acidic catalyst KU-1, mono- and diisopentenyl-p-cresols (I) and (II), the yield of which was 63%, were obtained.



Increasing the amount of KU-1 catalyst led to increased yields of pentenylcresol cyclization products (table, expt. 6). Alkenylation of o-cresol with piperylene in the presence of either zinc chloride deposited on aluminum oxide or cationite KU-1 at 100 and 150° temperatures occurred similarly. In the first case a mixture of acidic and neutral alkenylation products was formed: 2-methyl-4-(penten-3-yl-2)phenol (V), 2-methyl-4,6-di(penten-3-yl-2) phenol (VI), 3,7-dimethyl-3-ethylcoumaran (VII) and 2,4,8-trimethylchroman (VIII).



Alkenylation of o-cresol in the presence of cationite KU-1 at 100° led to formation of substituted cresols in a similar way (50%) and to a small amount of chroman (10%) (VIII). We did not isolate 2-methyl-6-(penten-3-yl-2) phenol from any of the experiments, apparently owing to its great cyclization tendencies. Thus, alkenylation of cresols with piperylene as a function of the nature of the catalyst used, the amount [of catalyst], and the experimental temperature can be directed either toward the formation of pentenylcresols or their cyclization products—the corresponding coumarans and chromans. Since none of the corresponding pentenyltolyl ethers were isolated in any of the experiments it is possible to conclude that alkenylation of cresols with piperlyene occurs exclusively as C-alkylation, but coumarans and chromans are conversion products from the pentenylcresols formed initially. The alkenylation of cresol methyl ethers, which leads to formation of the corresponding alkenyl ethers, is confirmation of the direct C-alkenylation. We previously established the structure of the pentenyl radical by alkenylation of m-cresol with piperlene [1].

EXPERIMENTAL

The alkenylation was conducted both at atmospheric pressure (with ethylsulfuric acid) and in an autoclave (with zinc chloride and KU-1) under a vapor pressure not exceeding 2-3 atm. The product obtained was dissolved in ether and washed with an aqueous sodium hydroxide solution and Claisen's solution for removal of the acidic portion of the product. After their separation the neutral and phenolic portions were distilled under vacuum through a column of 20 theoretical plates efficiency. Results of the alkenylation experiments are given in the table.

The following were separated from the acid portion of the product from alkenylation of p-cresol with piperylene:

1. 4-Methyl-2-(penten-3-yl)phenol: b.p. 127-129° (9 mm); n_D^{20} 1.5337; d_4^{20} 0.9777. Literature data [4]: b.p. 134-135° (13 mm); d_{15}^{15} 0.982. Melting point of the phenoxy derivative: 99-100°. Found: C 71.23; 71.36; H 7.78, 7.83%. $C_{14}H_{18}O_3$. Calculated: C 71.76; H 7.69%. Methyl ether: b.p. 110-112° (8 mm); n_D^{20} 1.5180; d_4^{20} 0.9431. 4-Methoxyisophthalic acid melting at 258-260° was obtained by oxidation of the methyl ether. Literature data [5,6]: m.p. 261°.

2. 4-Methyl-2,6-di-(penten-3-yl)phenol: b.p. 164-165° (9 mm); n_D^{20} 1.5287; d_4^{20} 0.9489. Literature data [4]: b.p. 171-173° (15 mm). Methyl ether: b.p. 156-157° (9 mm); n_D^{20} 1.5155; d_D^{20} 0.9304. 2-Methoxytrimesic acid m.p. 246-247° was obtained by oxidation of the methyl ether. Literature data [5,6]: m.p. 248°. From the neutral fraction of the product obtained by alkenylating p-cresol with piperylene were isolated.

TABLE. Results of Alkenylation Experiments of p- and o-Cresols With Piperylene

Expt. no.	Cresol used	Molar ratio cresol:piperylene	Catalyst	Amount of catalyst	Temp. °C	Time, hrs	Yield of alkenylation products, % of theoretical					
							Overall yield	Pentenylcresol	Dipentenylcresol	Dimethylethylcoumaran	Trimethylcoumaran	Neutral B.p.
1	p-cresol	1.7:1	$C_2H_5OSO_3H$	30	50	3	81.4	–	–	25.4	24.6	31.4
2	"	1.5:1	$ZnCl_2/Al_2O_3$	10	150	8	66.7	–	–	20	18.3	28.4
3	"	1:1	KU-1	10	90	8	10.7	3.2	4.6	–	–	2.9
4	"	1:1	KU-1	10	100	8	55.0	21	34	–	–	–
5	"	1:1	KU-1	10	120	8	67.6	23.6	40	–	–	4
6	"	1:1	KU-1	20	100	8	71.7	–	–	17.3	18.3	36.1
7	o-cresol	1.5:1	$ZnCl_2/Al_2O_3$	10	150	8	80.6	28	–	16	Trace	36.6
8	"	1.5:1	KU-1	10	100	8	85.0	38	10.8	Trace	10.6	25.6

3. 3,5-Dimethyl-2-ethylcoumaran: b.p. 104.106° (9 mm); n_D^{20} 1.5190; d_4^{20} 0.9791. Literature data [4]: b.p. 118-120° (15 mm).

4. 2,4,6-Trimethylchroman: b.p. 91-93° (3 mm); n_D^{20} 1.5219; d_4^{20} 0.9857; found MR 54.5. By alkenylation of o-cresol with piperylene the following were isolated from the acidic fraction:

5. 2-Methyl-4-(penten-3-yl-2)phenol: b.p. 92-93° (1 mm); n_D^{20} 1.5320; d_4^{20} 0.9831; found MR 55.7. $C_{12}H_{16}O\,|_{=4}$. Calculated MR 55.1. The phenoxy derivative melted at 91-92°. Found: C 71.78; 71.58; H 7.81; 7.95% · $C_{14}H_{18}O_3$. Calculated: C 71.76; H 7.69%. Methyl ether: b.p. 76-77° (1 mm); n_D^{20} 1.5173; d_4^{20} 0.9508. 4-Methoxyisophthalic acid melting at 259-260° was obtained by oxidizing the methyl ether.

6. 2-Methyl-4,6-di(penten-3-yl-2)phenol: b.p. 120-122° (1 mm); n_D^{20} 1.5273; d_4^{20} 0.9510; found MR 78.94. $C_{17}H_{25}O\,|_{=5}$. Calculated MR 78.7. Methyl ether: b.p. 114-117° (1 mm); n_D^{20} 1.5167; d_4^{20} 0.9409. 2-Methoxytrimesic acid melting at 246-247° was obtained by oxidizing the methyl ether. From the neutral fraction were isolated:

7. 3,7-Dimethyl-2-ethylcoumaran: b.p. 64-66° (1 mm); n_D^{20} 1.5160; d_4^{20} 0.9761.

8. 2,4,8-Trimethylchroman: b.p. 76-80° (1 mm); n_D^{20} 1.5232, d_4^{20} 0.9740.

Alkenylation of p-and o-cresol methyl ethers with piperylene was carried out in an autoclave in the presence of zinc chloride. Two substances were obtained upon alkenylation of p-cresol methyl ether: A) b.p. 109-112° (9 mm); n_D^{20} 1.1565 and d_4^{20} 0.9354, which on oxidation gave 4-methoxyisophthalic acid (m.p. 260-261°) and B) b.p. 156-157° (9 mm); n_D^{20} 1.5138 and d_4^{20} 0.9248, by oxidation of which 2-methoxytrimesic acid (m.p. 246-247°) was obtained.

Upon alkylating o-cresol methyl ether with piperylene were obtained C) b.p. 76-79° (1 mm); n_D^{20} 1.5190 and d_4^{20} 0.9450, and D) b.p. 118-120° (1 mm); n_D^{20} 1.5178 and d_4^{20} 0.9358, by oxidation of which were obtained, respectively, 4-methoxyisophthalic and 2-methoxytrimesic acids.

SUMMARY

1. The alkenylation of p- and o-cresols with piperylene in the presence of acid catalysts was studied.

2. Under the conditions used the reaction between p- and o-cresol and piperylene occurs as C-alkenylation.

3. The reaction products between p- and o-cresol and piperylene are isomeric mono- and diisopentenylcresols and their cyclization products—substituted chromans and coumarans.

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ALKYLATION OF PHENOLS WITH MIXED-FUNCTIONAL COMPOUNDS

2. ALKENYLATION OF o- and p-CRESOLS WITH ALLYL ALCOHOL

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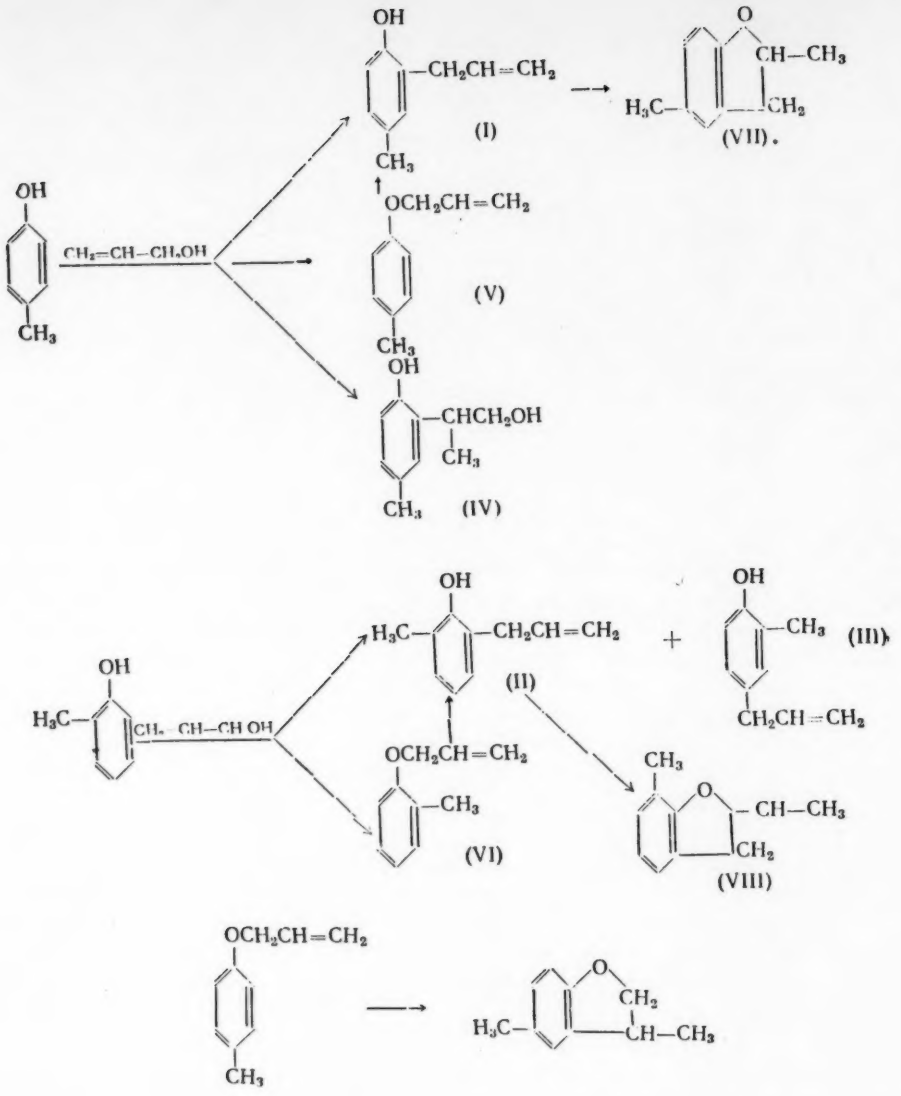
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9,
pp. 1660-1665, September, 1961
Original article submitted March 29, 1961

We previously described [1] the alkenylation of m-cresol with allyl alcohol in the presence of acidic catalysts—phosphoric acid and zinc chloride deposited on aluminum oxide. We separated 3-methyl-6-allylphenol, 3-methyl-4-allylphenol, and 2,6-dimethylcoumaran from these reaction products. Only 3-methyl-6-allylphenol and a neutral reaction product—2,6-dimethylcoumaran- and m-cresol allyl ether—were obtained by alkenylating m-cresols allyl alcohol in the presence of cationite KU-1. In this paper we will present the results of allylating o- and p-cresols in the presence of the same catalysts. As was shown, allylation of o- and p-cresols occurred at a higher temperature than in the case for m-cresol. Moreover, high yields of alkenylation products were obtained in the presence of zinc chloride deposited on aluminum oxide. Use of this catalyst made possible isolating good yields of alkenylcresols and of neutral substances and also substantially decreased the formation of high-boiling products. The latter contains a considerable quantity of polymer, which is depolymerized during distillation, but the dipolymerization is accompanied by considerable tar formation.

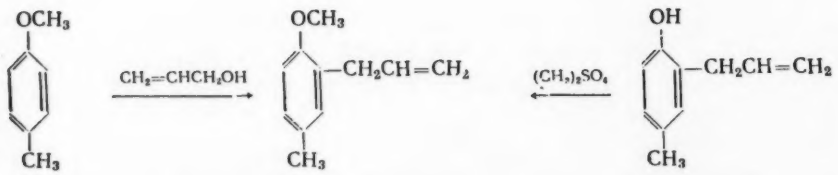
Study of the phenolic fraction of the product showed that, besides the o- and p-cresols used, it contained isomeric alkenylcresols. Methyl ethers, oxidation of which led to the corresponding methoxyphthalic acids, were obtained from these. It was established that allyl-p-cresol had the structure 4-methyl-2-allylphenol (I), but that allyl-o-cresol occurred in two isomeric forms—2-methyl-6-allylphenol (II) and 2-methyl-4-allylphenol (III). The properties of the latter agreed with the properties of allylcresols obtained by rearrangement of the corresponding allyltolyl ethers.

In the products from some allylation experiments with p-cresol in the presence of phosphoric acid and cationite KU-1 at 120° a small amount (3-7%) of a substance which apparently was 2-(3-methyl-6-hydroxyphenyl)propanol-1 (IV) was found besides 4-methyl-2-allylphenol. In support of this supposition the oxidation product of its methyl ether, analytical data for its phenoxy derivative, and determination of the number of active hydrogen atoms are presented. Formation of this substance indicates an alkylation reaction not only on the hydroxyl group but also on double bond of allyl alcohol, which other authors have not observed [2-6]. In our previous work on phenolallylation [2-6] we noted the formation of neutral oxygen compounds. We separated the corresponding allylation products from p- and o-cresols: allyl-p-tolyl ether (V), allyl-otolyl ether (VI), and also 2,5-dimethylcoumaran (VII) and 2,7-dimethylcoumaran (VIII).

Allyltolyl ethers (V) and (VI) separated from the product undergo isomerization under the experimental conditions in the presence of phosphoric acid or zinc chloride deposited on aluminum oxide. Thus, 2,5- and 2,7-dimethylcoumarans (VII) and (VIII) were obtained. Under similar conditions 4-methyl-2-allylphenol (I) and 2-methyl-6-allylphenol (II) and (VIII). Formation of the latter indicates that in the alkenylation process cyclization of the ether doesn't occur directly, but cyclization of the allylphenols formed by their rearrangement occurs since in the first case the dimethylcoumaran being formed has a different structure, for example:



Allylation of p-cresol methyl ether led to 4-methyl-2-allylphenol methyl ether, which we obtained by the following methylation:



Thus, based on o- and p-cresols it was shown that the allylation reaction proceeds under these conditions in two directions: 1) direct C-allylation and 2) O-allylation with subsequent isomerization of the allycresol ethers formed.

EXPERIMENTAL

p-Cresol: b.p. 197-198° (750 mm); m.p. 35-36°. o-Cresol: b.p. 191-192° (750 mm); m.p. 31°. Allyl alcohol: b.p. 96-97° (760 mm); n_D^{20} 1.4136; d_4^{20} 0.8578. All substances used in the experiments were purified by simple treat-

ments of commercial preparations. The catalysts, the apparatus, and the methods for studying catalysts were described in an earlier communication [1]. The results of allylating p- and o-cresols in the presence of the indicated catalysts are given in Tables 1 and 2. In Table 3 the properties of the substances we separated from allylation products of p- and o-cresols are presented.

TABLE 1. Results of Catalytic Allylation of p-Cresol

Catalyst	Amt. of catalyst, % of substance used	Temp, °C	Reaction time hrs	Yield of products, %	Total yield of allylation products		Yield of allylation products, % on reacted p-cresol				
					% of theoret.	% on reacting cresol	allyl-p-tolyl ether	2,5-dimethylcoumaran	4-methyl-2-allylphenol	2(3-methyl-6-hydrophenyl) propanol-1	High boiling polymers
H_3PO_4	200	95—100	10	79,6	57,6	80,1	0,3	4,3	2,1	7,4	66,0
H_3PO_4	200	115—120	10	77,7	62,0	86,5	—	1,0	0,8	9,7	75,0
KU-1	10	95—100	10	73,2	22,7	68	1,1	6,8	—	—	60,1
KU-1	10	120	10	83,4	51,0	88	0,5	15,7	1,4	5,0	65,4
$ZnCl_2/Al_2O_3$	10	150	6	74,3	14,3	76,9	1,1	31,5	10,0	—	34,3
$ZnCl_2/Al_2O_3$	10	180—190	10	70,0	42,0	79,9	0,4	20,8	19,0	—	39,7

TABLE 2. Results of Catalytic Allylation of o-Cresol

Catalyst	Amt. of catalyst, % of substance used	Temp, °C	Time of reaction hrs	Yield of product, %	Total yield of allylation products		Yield of allylation products, % of reacting o-cresol				
					% of theoret.	% of reacting cresol	Allyl-o-tolyl ether	2-7, dimethylcoumaran	2-Methyl-6-allylphenol	4-Methyl-6-allylphenol	High boiling products and polymers
H_3PO_4	200	75	9	81,3	67	56,3	—	8,2	9,8	21,9	16,4
H_3PO_4	200	100	9	80	48,8	79,2	—	5,5	3,3	9,9	60,5
H_3PO_4	200	110—115	9	76,8	57,9	88,1	—	6,7	1,9	10,6	68,9
$ZnCl_2/Al_2O_3$	10	125	10	84,2	20,2	48,7	4,8	2,4	21,9	14,8	4,8
$ZnCl_2/Al_2O_3$	10	150	10	82,3	28,3	63,75	3,4	4,5	22,7	18,4	14,75
$ZnCl_2/Al_2O_3$	10	175	10	80,1	30,8	63,6	—	10,2	10,4	20	23
KU-1	10	100	10	86,7	16,4	62,2	15,6	10,4	5,2	Trace	32
KU-1	10	120	10	83,2	57,2	80,6	6	15,7	2,9	—	56

TABLE 3. Properties of Substances Separated from Allylation Products of p- and o-Cresols

No. of substances	Substance	B.p. °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.	M.p. of phenoxy derivative, °C
I	4-Methyl-2-allylphenol	98—100(7)	1,5410	1,0087	45,50	45,83	122—123
II	2-Methyl-6-allylphenol	76— 78(4)	1,5380	1,0140	45,66	45,83	
III	2-Methyl-4-allylphenol	92— 94(4)	1,5389	1,0144	45,71	45,83	113—114
IV	2-(3-Methyl-6-hydroxyphenyl)propanol-1	114—116(7)	1,5609	1,0122	48,34	48,27	84—84,5
V	Allyl ether of p-cresol	80— 82(7)	1,5204	0,9712	46,33	45,96	
VI	Allyl ether of o-cresol	64— 65(4)	1,5187	0,9680	46,31	45,96	
VII	2,5-Dimethylcoumaran	88— 90(9)	1,5249	1,0040	45,17	44,22	
VIII	2,7-Dimethylcoumaran	92— 93(11)	1,5285	1,0051	45,31	44,22	

The literature data for 4-methyl-2-allyl phenol are [7]: b.p. 79-80° (2 mm); n_D^{20} 1.5405; d_4^{20} 1.0120; 2-methyl-4-allylphenol [8]: b.p. 106-107° (12 mm); d_{15} 1.0070; allyl ether of p-cresol [7]: b.p. 102° (17 mm); n_D^{20} 1.5204; d_4^{20} 0.9726; allyl ether of o-cresol [8]: b.p. 85° (12 mm); d_{15} 0.969; 2,5-dimethylcoumaran [9]: b.p. 99-99.5° (14 mm); n_D^{20} 1.5251; 2,7-dimethylcoumaran [10]: b.p. 92-93° (13 mm); $d_4^{18.5}$ 1.0150; $n_D^{18.5}$ 1.530.

For phenols I-IV indicated in Table 3 methyl ethers with the following properties were obtained: I) b.p. 87-88° (6 mm); n_D^{20} 1.5212; d_4^{20} 0.9595; MR 51.40. II) b.p. 72-73° (5 mm); n_D^{20} 1.5170; d_4^{20} 0.9597; MR 51.30. III) b.p. 78-80° (5 mm); n_D^{20} 1.5182; d_4^{20} 0.9615; MR 51.31. IV) b.p. 104-108° (7 mm); n_D^{20} 1.5470; d_4^{20} 0.9760; MR 58.52.

An acid melting at 259-260°, which corresponds to the melting point of 4-methoxyisophthalic acid (260°) [12] was obtained by oxidation of the methyl ethers of phenols I, III, and IV with permanganate solution [11]. An acid melting at 218-219°, which is the melting point of 2-methoxyisophthalic acid (220°) [12] was obtained by oxidizing the methyl ether of phenol II. For identification of phenols I and II (see Table 3) their synthesis by rearrangement of corresponding allyl ethers under conditions described by Claisen [13] was carried out; the properties of the phenols and their phenoxy derivatives corresponded completely.

The phenoxy derivative of 2-methyl-4-allylphenol melted at 113-114°. Found: C 69.88; 69.59; H 7.67; 7.55% $C_{12}H_{14}O_3$. Calculated: C 69.90; H 7.69%. The phenoxy derivative of 2-(3-methyl-6-hydroxyphenyl)propanol-1 melted at 84-84.5°. The number of active hydrogen atoms by the Terent'ev micromethod was two [14].

Rearrangement of the allyl ethers separated from the product under conditions Claisen described led to formation of 4-methyl-2-allylphenol (A) from allyl p-tolyl ether and 2-methyl-6-allylphenol (B) from allyl o-tolyl ether. A) b.p. 99-100° (7 mm); n_D^{20} 1.5401; d_4^{20} 1.0051. melting point of phenoxy derivative 122-122.5°; B) b.p. 79-80° (4 mm); n_D^{20} 1.5380; d_4^{20} 1.0142.

Rearrangement of the indicated ethers in the presence of either phosphoric acid or zinc chloride deposited on aluminum oxide led only to the formation of 2,5-dimethylcoumaran (VII) and 2,7-dimethylcoumaran (VIII) under these experimental conditions. 2,5-Dimethylcoumaran (VII): b.p. 80-80.5° (6 mm); n_D^{20} 1.5250; d_4^{20} 1.0055. 2,7-Dimethylcoumaran: b.p. 86-88° (9 mm); n_D^{20} 1.5289; d_4^{20} 1.0056.

Alkenylation of p-Cresol Methyl Ether with Allyl Alcohol. Alkenylation of the methyl ether with allyl alcohol was conducted in the presence of phosphoric acid at 95-100° for 8 hr. From the product were separated 5.2 g of a substance boiling at 82-84° (5 mm); n_D^{20} 1.5198; d_4^{20} 0.9620 with properties close to those of 4-methyl-2-allylphenol methyl ether (see Table 3). Moreover, 31.8 g of a crystalline substance boiling at 169-170° (6 mm) and melting at 72-72.5° was obtained. Found: C 80.37; 80.65; H 8.43, 8.55%, which corresponds to the formula $C_{19}H_{24}O_2$. Evidently the substance isolated has the structure 1,2-di(3-methyl-6-methoxyphenyl) propane.

Cyclization of 4-Methyl-2-allylphenol. A mixture of 10 g of allyl-p-cresol and 12 g of phosphoric acid was heated with vigorous stirring for 6 hr at 115-120°. Only 2 g of 2,5-dimethylcoumaran [b.p. 82.5-84° (7 mm)]; n_D^{20} 1.5245; d_4^{20} 1.0055 was separated from the reaction products. Literature data for the properties of 2,5-dimethylcoumaran [9]: b.p. 99-99.5° (14 mm); n_4^{20} 1.5251.

SUMMARY

1. The alkenylation of o- and p-cresols with allyl alcohol in the presence of acid catalysts was studied.

2. The reaction occurs by two paths: C- and O-allylation.

3. Isomeric allyl cresols, their cyclization products—the corresponding coumarans—and allyltolyl ethers are the allylation products.

4. The formation of an allylation product of cresols with the double bond of allyl alcohol—2-(3-methyl-6-hydroxyphenyl)propanol-1—was observed for the first time.

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INVESTIGATION OF THE CATALYTIC PROPERTIES OF RARE EARTH OXIDES

COMMUNICATION 2. CONVERSION OF CYCLOHEXENE, 1-METHYLCYCLOHEXENE-1 and n-HEPTENE-1 ON ERBIUM OXIDE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1665-1669, September, 1961
Original article submitted December 13, 1960

Until now the conversion of cycloolefinic hydrocarbons on rare earth oxides has not been investigated. When extending the study of the catalytic properties of rare earth oxides we decided to examine the behavior of some cycloolefins on Er_2O_3 and Er_2O_3/Al_2O_3. An analysis of the obtained products by means of gas-liquid chromotography showed that these catalysts differ in the respect that pure erbium oxide does not give isomerization of a six- to a five-ring, whereas this isomerization does occur on the catalyst consisting of erbium and aluminium oxide. Both these catalysts dehydrogenate the original cyclenes to the corresponding aromatic hydrocarbons and shift the double bond in the ring. It should be noticed that under the conditions used they do not effect disproportionation of hydrogen. So, these investigations showed that erbium oxide is a dehydrogenation catalyst and displaces the double bond in the ring.

Under the conditions used (500°) on both catalysts n-heptene-1 is partly cyclized into toluene, isomerized into other heptenes and, moreover, on the mixed catalyst it is converted into saturated C_7 hydrocarbons.

EXPERIMENTAL

As catalysts in this investigation we used pure erbium oxide and 15% erbium oxide on aluminum oxide. In all experiments the reactor tube was filled with 10ml catalyst. The way of preparing the catalysts, the experimental conditions and the method of analyzing the products have been described in the preceding paper [1].

Cyclohexene was obtained by heating cyclohexanol with concentrated sulfuric acid. 1-Methylcyclohexene-1 was synthesized by reacting cyclohexanol with magnesium methyl iodide and then dehydrating the 1-methylcycohexanol-1-iodide. n-Heptene-1 was prepared ny pyrolyzing heptyl acetate at 510°. The characteristic constants of the synthesized hydrocarbon are given in Table 1.

TABLE 1. Properties of the Original Hydrocarbons

Hydrocarbons	Our data			Literature data		
	B.p., °C at 760 mm	n_D^{20}	d_4^{20}	B.p., °C at 760 mm	n_D^{20}	d_4^{20}
Cyclohexene	82,8	1,4457	0,8086	82,6	1,4464	0,8094 [2]
1-Methylcyclohexene-1	109,2	1,4494	0,8092	110	1,4503	0,8102 [3]
n-Heptene-1	93,2	1,3993	0,6965	93,6	1,3998	0,6970 [4]

When cyclohexene and 1-methylcyclohexene-1 were passed over Er_2O_3, the yield of liquid products remained constant with time and amounted to 80.7 and 83.4%, respectively. The liquid products obtained in these experiments did not contain hydrocarbons with a molecular weight higher than that of the original substance. The chromatograms of the gas showed that the latter consisted of 90-96% hydrogen and 4-10% C_1-C_4 hydrocarbons, whereas in the first hours of operation a gas was obtained, which was more rich in hydrocarbons than that in the later hours. On this catalyst the formation of coke was neglegible. So, after operating six hours with cyclohexene 0.13 g coke (0.93% of the catalyst weight) had been deposited on the catalyst, in the case of 1-methylcyclohexene-1 after 17 hr 0.21 g coke

(1.5% of the catalyst weight) had been formed. The product obtained in the experiment with cyclohexene on Er_2O_3 consisted of benzene and cyclohexene, while the benzene content changed little (from 20 to 23%) in the course of the experiment. In a chromatographic analysis the product obtained from 1-methylcyclohexene-1 over Er_2O_3 gave three peaks; the first of them was identified as a mixture of 1-methylcyclohexene-2 and 1-methylcyclohexene-3, the second as the original 1-methylcyclohexene-1 and the last one belonged to toluene. According to data in the literature [5], 1-methylcyclohexene is easily separated from 1-methylcyclohexene-2 and -3, the separation of which is much more difficult.

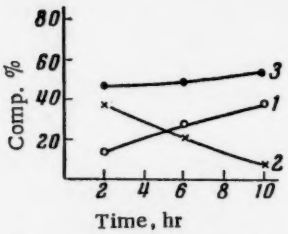

Fig. 1. Composition of the reaction product plotted versus time (Er_2O_3, 1-methylcyclohexene-1); 1) toluene; 2) 1-methylcyclohexene-2 and -3; 3) 1-methylcyclohexene-1.

Data obtained in the conversion of 1-methylcyclohexene-1 over Er_2O_3 are given in Table 2 and Fig.1.

Upon converting cyclohexene and 1-methylcyclohexene-1 over Er_2O_3/Al_2O_3 the yields of liquid products increased with time. So, in the case of methylcyclohexene this yield amounted to 60.2% after the first two hours of operation and to 75.3% after 9-10 hr. Later on the latter value did not change. The gases taken for an analysis consisted of 85-93% hydrogen and 7-15% C_1-C_4 hydrocarbons, whereas, just as in the case of Er_2O_3, at the start of the experiment the gas was more rich in hydrocarbons. In the course of the experiments much more coke was formed on this catalyst than on Er_2O_3. So, in the experiment with cyclohexene the amount of coke deposited in six hours was 0.49 g (4% of the catalyst weight) and in the case of 1-methylcyclohexene-1 it was 0.73 g (6% of the catalyst weight). A distillation of the liquid products showed that they contained ~15% hydrocarbons with a boiling point higher than that of benzene and toluene. The composition of the product obtained by passing cyclohexene over Er_2O_3/Al_2O_3, as was derived from a chromatographic analysis, is given in Table 3.

TABLE 2. Conversion of 1-Methylcyclohexene-1 over Er_2O_3 at 515° as a Function of the Time during which the Catalyst was in Operation, %

Product composition	Time of operation		
	1–2	5–6	9–10
Toluene	13.9	27.8	38.4
1-Methylcyclohexene-2 and -3	38.9	23.4	7.2
1-Methylcyclohexene-1 (substance fed)	46.8	48.6	54.4
Sum of all methylcyclohexenes	86.0	72.0	61.6
Degree of conversion in %	53.2	51.4	45.6
Selectivity of dehydrogenation in %	26.4	54.5	84.3
Selectivity of isomerization in %	73.6	45.5	15.7

TABLE 3. Conversion of Cyclohexene on Er_2O_3/Al_2O_3 at 515° as a Function of the Time during which the Catalyst was in Operation, %

Product composition	Time of operation		
	1–2	3–4	5–6
Benzene	17.5	10.9	11.2
Methylcyclopentenes	63.0	60.6	56.7
Cyclohexene	19.5	28.5	32.1
Degree of conversion in %	80.5	71.5	67.9
Selectivity of isomerization in %	78.3	84.8	83.5
Selectivity of dehydrogenation in %	21.7	15.2	16.5

The products obtained by passing methylcyclohexene over Er_2O_3/Al_2O_3 could be identified only partially. In this case ring isomerization leads to dimethylcyclopentenes so that the chromatogram became quite complicated. From the chromatogram of the product collected during the first two hours it was found that the said porduct to 63% consisted of toluene.

In experiments with n-heptene-1 the total yield of products for Er_2O_3 and Er_2O_3/Al_2O_3 was 74.5 and 68.3%, respectively. The gas collected during the reaction of n-heptene over Er_2O_3 and Er_2O_3/Al_2O_3 had the following composition (in vol. %):

	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8
Er_2O_3	66.4	7.8	5.6	6.0	0.9	6.9	0.3	4.8
$ErCO_3/Al_2O_3$	59.5	4.6	1.9	11.3	0.8	16.0	0.3	5.4

As is evident from these data, the gas obtained in the catalytic conversion of n-heptene-1 over Er_2O_3/Al_2O_3 contained two times more unsaturated hydrocarbons than that obtained over Er_2O_3.

In the liquid products obtained on Er_2O_3 and Er_2O_3/Al_2O_3 the amount of toluene found was 6 and 8.5%, respectively. In the chromatogram for the product obtained over Er_2O_3/Al_2O_3 six peaks, besides that of toluene, were detected in the region belonging to C_7 hydrocarbons, whereas in the case of Er_2O_3 there were only two of them. The content of unsaturated hydrocarbons in the product (as derived from the iodine number) was 91.8 and 47.0% in the case of Er_2O_3 and Er_2O_3/Al_2O_3, respectively. So, on Er_2O_3/Al_2O_3 the conversion of the original hydrocarbon is a more complex reaction than on Er_2O_3.

In Fig.2 the refractive index of the product obtained in the conversion of cyclohexene and 1-methylcyclohexene-1 on Er_2O_3 and Er_2O_3/Al_2O_3 is plotted as a function of time. It should be noticed that in the conversion over Er_2O_3 of both cyclohexene and 1-methylcyclohexene-1 in the liquid products there are no hydrocarbons with a molecular weight higher than that of the original substance and, therefore, a change in n_D^{20} expresses a change in the content of C_6 (see Table 3) and C_7 (see Table 2) hydrocarbons in the reaction product.

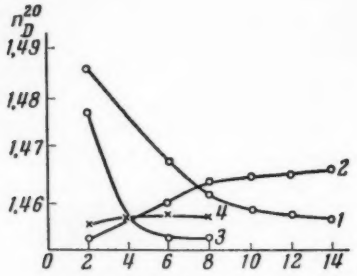

Fig. 2. Refractive index n_D^{20} as a function of time (515°):
Er_2O_3 1) 1-methylcyclohexene-1; 3) cyclohexene; Er_2O_3/Al_2O_3 2) 1-methylcyclohexene-1; 4) cyclohexene.

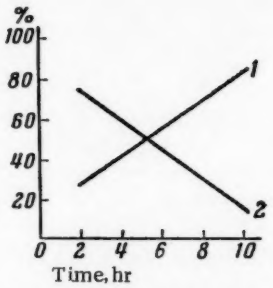

Fig. 3. Selectivity with respect to dehydrogenation (1) and displacement of the double bond (2) (1-methylcyclohexene-1, Er_2O_3 515°).

When, however, the conversion of those same hydrocarbons is carried out over Er_2O_3/Al_2O_3, a change in n_D^{20} not only expresses a change in the content of C_6 and C_7 products, but is characterized to a considerable extent by the occurrence of hydrocarbons with a higher molecular weight. In fact, in the course of time the yields of products increase at the same rate at which n_D^{20} falls, the formation of gas drops and the products become more light-colored.

In Fig.1 and Table 2 it is shown how the composition of the products obtained by passing 1-methylcyclohexene-1 over Er_2O_3 changes with time. As is evident from the curves in Fig.1, the content of dehydrogenation product (toluene) increases in the course of time from 14 to 38%, at the same time the content of 1-methylcyclohexene-2 and -3 falls from 39 to 7%, whereas the amount of unchanged 1-methylcyclohexene-1 rises from 47 to 54%. So, in the course of time the activity of Er_2O_3 with respect to dehydrogenation increases and that with respect to displacement of the double bond decreases. When one looks at Fig.3, it is evident that the selectivity with respect to dehydrogenation of the original hydrocarbon increases from 26 to 84%, whereas that with respect to displacement of the double bond decreases from 74% to 16%.

SUMMARY

1. Catalytic conversion of cyclohexene, 1-methylcyclohexene-1 and n-heptene-1 has been investigated on Er_2O_3 and Er_2O_3/Al_2O_3 at 510-515°.

2. Both catalyst effect dehydrogenation of the six-ring cyclenes and displacement of the double bond in the ring. Moreover, on Er_2O_3/Al_2O_3 isomerization of the six-ring to a five-ring takes place.

3. n-Heptene-1 at 500° over Er_2O_3 and Er_2O_3/Al_2O_3 is partly dehydrogenized under cyclization to toluene, isomerized to other heptenes and on Er_2O_3/Al_2O_3 it is partly converted into saturated hydrocarbons.

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INVESTIGATION INTO THE EFFECT OF THIOPHENE ON THE CATALYTIC ACTIVITY OF AN INDUSTRIAL ALUMINIUM-MOLYBDENUM CATALYST

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9 pp. 1669-1672, September, 1961
Original article submitted January 2, 1961

Nowadays, the aluminium-molybdenum catalyst is very widely used in the oil processing industry for obtaining concentrates of aromatic hydrocarbons and producing fuels with a high octane number. It is known that in the course of time this catalyst quite rapidly looses its activity and, therefore, it requires frequent regenerations. The reason why aluminum-molybdenum and aluminium-chromium catalysts too are rapidly deactivated lies in the fact that their surfaces are covered by decomposition products of the hydrocarbons treated. However, in the literature, with the exception of one paper, there are no data on the effect of sulfur compounds on the catalytic activity of an aluminium-molybdenum catalyst.

In a paper by Hummer and Taylor [1] the effect of thiophene on the activity of aluminium-molybdenum and aluminium-chromium catalysts in the dehydrocyclization of n-heptane was investigated at 470° in a current of hydrogen. These authors established that, when n-heptane containing 0.5 mole % thiophene was fed, the activity of the aluminium-chromium catalyst falls much more rapidly than does that of the aluminium-molybdenum catalyst. Moreover, they proved that on the aluminum-chromium catalyst most of the thiophene introduced is decomposed to hydrogen sulfide, whereas on the aluminium-molybdenum catalyst ~30% of the thiophene remains on the surface in the form of molybdenum sulfide.

In the present study we undertook to examine the rate at which an aluminium-molybdenum catalyst is deactivated, when it is operated with pure hydrocarbons or with hydrocarbons containing various amounts of thiophene. In order to estimate quantitatively the sulfur content on the catalyst we used thiophene tagged by the radioisotope S^{35}. Moreover, it was interesting to compare the data obtained by investigating this catalyst with the results obtained by studying the poisoning of platinum catalysts [2-4].

EXPERIMENTAL

All experiments on the dehydrogenation of cyclohexane and the dehydroclization on n-hexane on an industrial aluminium-molybdenum catalyst were carried out in a catalytic equipment of the usual type at atmospheric pressure in a current of hydrogen. The original hydrocarbons were purified and their degree of purity was determined in a gas-liquid chromatograph. As poisons we used normal thiophene and thiophene containing S^{35}.

Before starting the experiments each catalyst portion in the amount of ~12 g (~17 ml) was heated at 500° in a current of hydrogen during six hours. After that both the pure hydrocarbon and that contaminated by various amounts of thiophene were fed at a space velocity of 0.2 hr^{-1} and a molar ratio H_2:HC = 5:1. The experiments lasted from six to 45 hours. In order to follow the change in the activity of the catalyst in the dehydrogenation of cyclohexane and the dehydrocyclization of n-hexane at fixed intervals of time we took product samples, the compositions of which were determined by means of gas-liquid chromatography. In all experiments the hydrogen sulfide contained in the gas leaving the apparatus was removed in the form of zinc sulfide and its amount was determined iodometrically [2]. After the experiment had been stopped, all product samples taken were poured together and in the combined product the sulfur content was determined. In order to determine the amount of sulfur deposited on the catalyst in the course of the experiment we used the radiochemical method described in our preceding paper [3]. Samples of the catalyst, from which targets were prepared, were taken 4, 11, and 20 hr after the start of the experiment with a mixture of cyclohexane and 1.5% thiophene containing radiosulfur-35.

The results obtained in experiments on the dehydrogenation of cyclohexane at 488° and the dehydrocyclization of n-hexane at 500° have already been reported previously [5]; therefore, they will be used only for a comparison with the data obtained in the present study. Data obtained upon dehydrogenating cyclohexane containing 1.0; 1.5; 2.0; 3.0; and 5.0 weight % thiophene are given in Table 1. From these data it is evident that during the experiment with mixtures of cyclohexane and thiophene the aromatization ability of the catalyst falls sharply in the first hours of operation and after that the rate of deactivation decreases gradually. From the same table it follows that the catalyst studied is deactivated to a greater extent, when the thiophene concentration in the cyclohexane fed is raised. In Fig. 1 curves indicating the poisoning of the catalyst by thiophene are shown together with data obtained in operation with pure cyclohexane [5]. From these curves it is evident that the rate at which the catalyst is deactivated by the products of a thorough cleavage of cyclohexane is much smaller than the rate at which its aromatization activity is lowered by thiophene. It should be noticed that the shape of the poisoning curves for the aluminium-molybdenum catalyst and also the way in the hydrocarbon fed (Fig.2) has about the same character as is also found in the curves which we previously obtained for a platinum-aluminium oxide catalyst [2-4]. It should be pointed out that in the case of the aluminium-molybdenum catalyst the curve region corresponding to a stabilized aromatization activity, the magnitude of which depends upon the thiophene concentration, is less clearly developed. Obviously, this fact may be explained as a deactivation of this catalyst caused by the simultaneous action of thiophene and a considerable formation of coke taking place on the surface.

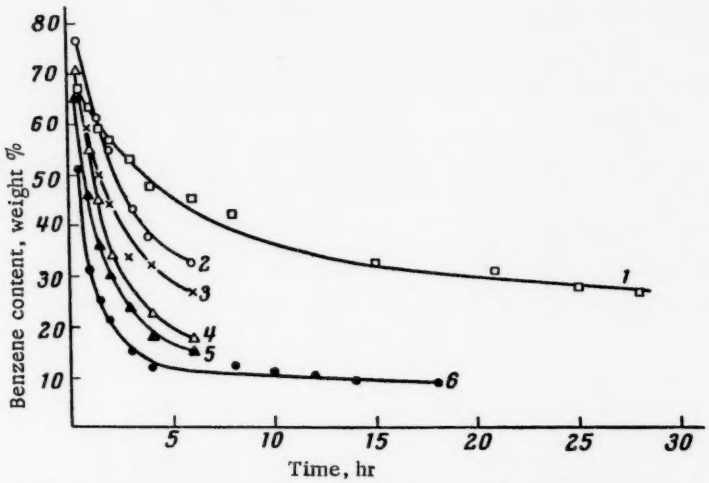

Fig. 1. Change in the benzene content of the products obtained when mixtures of cyclohexane with various amounts of thiophene are dehydrogenated: 1) pure cyclohexane; 2) 1.0 weight % thiophene; 3) 1.5 weight% thiophene tagged by S^{35}; 4) 2.0 weight % thiophene; 5) 3.0 weight % thiophene; 6) 5.0 weight % thiophene.

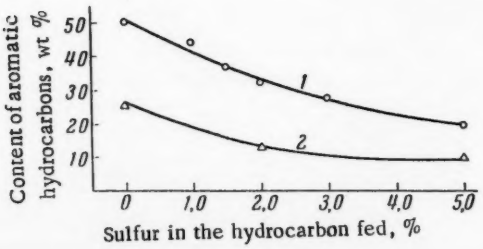

Fig. 2. The aromatization activity of the aluminium-molybdenum catalyst plotted versus the thiophene concentration in the hydrocarbon fed: 1) cyclohexane; 2) n-hexane.

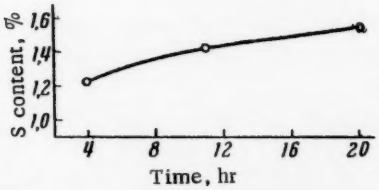

Fig. 3. Change in the amount of sulfur deposited on the catalyst in the dehydrogenation of cyclohexane containing 1.5% thiophene tagged by radiosulfur-S^{35}.

In the experiment with cyclohexane containing 1.5% thiophene tagged by radiosulfur-35 it was found that the amount of sulfur deposited on the catalyst increases gradually, as is indicated in Fig.3. After 20 hours operation the amount of sulfur on the catalyst attains 1.6% of the weight of the latter and this is equal to 28.1% of the amount of sulfur fed. Meanwhile, the liquid products obtained in the course of the experiment contain 7.9% and with the gas ~62.5% of the total amount of sulfur fed is removed in the form of hydrogen sulfide.

TABLE 1. Change of the Benzene content in the Products obtained by Dehydrogenating Cyclohexane mixed with various amounts of Thiophene ($t = 488°$, $v = 0.2\ hr^{-1}$, $H_2 : HC = 5 : 1$)

Time at which the product was taken	Benzene content in the products for the following concentrations in the cyclohexane fed, weight %					
	0.0	1.0	1.5*	2.0	3.0	5.0
0,5	67,7	77,1	68,5	70,0	66,9	51,0
1,0	63,0	62,4	59,5	54,0	46,1	30,3
2,0	56,4	55,8	44,7	34,3	30,9	21,3
4,0	48,1	37,8	29,7	22,3	18,0	12,7
6,0	45,5	33,0	21,5	17,3	16,9	14,7
10,0	37,1	—	15,4	—	13,1	10,6
15,0	—	—	14,0	—	—	8,8
20,0	30,6	—	11,1	—	—	8,1
45,0	21,8	—	—	—	—	—

* Thiophene tagged by radiosulfur-35 was used.

TABLE 2. Change in the content of aromatic Hydrocarbons in the products obtained in the dehydrocyclization of n-hexane mixed with various amounts of Thiophene ($t = 520°$, $v = 0.2\ hr^{-1}$, $H_2 : HC = 5 : 1$)

Thiophene concentration in hexane fed, wt. %	Content of aromatic hydrocarbons in the products, weight %, after					
	1 hr	2 hr	3 hr	5 hr	10 hr	15 hr
0,0	59,1	52,4	41,6	35,3	27,0	24,8
2,0	44,2	28,7	22,4	15,1	—	8,1
5,0	30,2	17,4	11,3	8,0	8,1	—

Data on the way in which the activity of the catalysts changes in the dehydrogenation of n-hexane containing 2.0 and 5.0% thiophene are given in Table 2 and Fig.4. From these data it is evident that the aromatization ability of the aluminium-molybdenum catalyst in this case changes in exactly the same way as is found in the dehydrogenation of cyclohexane containing thiophene. It should be noticed that, when thiophene is present, the yield of alkylized aromatic, the formation of which from n-hexane has been reported previously [5], decreases simultaneously with the lowered yield of benzene. It must be pointed out that the qualitative composition of the products from cyclohexane and from n- hexane too in the presence of thiophene does not differ from the composition of the products obtained from the pure hydrocarbons on the same catalyst under identical conditions.

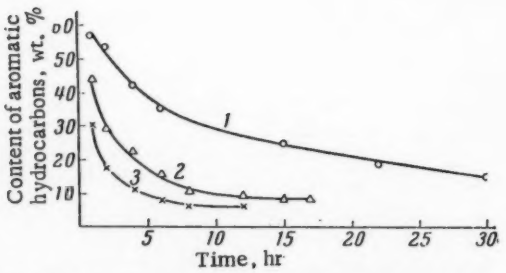

Fig. 4. Change in the content of aromatic hydrocarbons in the products obtained, when mixtures of n-hexane with various amounts of thiophene are dehydrogenated: 1) pure hexane; 2) 2.0 weight % thiophene; 3) 5.0 weight % thiophene.

SUMMARY

1. The effect of thiophene on the catalytic activity of an industrial aluminium-molybdenum catalyst in the dehydrogenation of cyclohexane and the dehydrocyclization of n-hexane has been investigated.

2. When thiophene is present, the deactivation of the aluminium-molybdenum catalyst proceeds much more rapidly than it does in runs with the pure hydrocarbons and the shape of the poisoning curves in the first parts of a run is similar to that of the curves obtained previously for platinum-aluminium oxide catalysts.

3. By means of a radiometric analysis it has been established that from the total amount of sulfur fed 28.1% is deposited on the catalyst, ~62.5% is eliminated in the form of hydrogen sulfide and 7.9% is contained in the liquid product.

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THE CATALYTIC PROPERTIES OF RHENIUM SULFIDE-ALUMNIA CATALYST IN THE DEHYDROGENATION OF CYCLOHEXANE UNDER PRESSURE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1673-1676, September, 1961
Original article received January 3, 1961

In our previous work [1] we have investigated the catalytic properties of a 20% rhenium-alumina catalyst treated with hydrogen sulfide in the following reactions: the dehydrogenation of cyclohexane, the dehydro-isomerization of methylcyclopentane, and the dehydrocyclization of n-hexane; the temperature used was 500-510°, the volume rate was 1.0 hr^{-1}, the pressure of hydrogen was 5 atm, and the ratio of hydrogen to hydrocarbon (H_2/HC), was 5:1. Under these conditions the hydrocarbons mentioned gave 76, 52, and 10% benzene. We have thought it a matter of interest to continue our investigations, and to study the catalytic properties of rhenium sulfide-alumina catalysts, containing a smaller quantity of rhenium.

Four catalyst samples have been prepared, containing 1, 5, 10, and 15% rhenium. The catalytic properties of these were investigated in the dehydrogenation of cyclohexane at 500°, using 5 atm hydrogen pressure, and a volume velocity of cyclohexane supply of 1.0 hr^{-1}, and a ratio H_2:HC of 5:1. Analysis of the catalyzates has shown that these catalysts possess both dehydrogenating and isomerizing properties, such that increase in the concentration of rhenium in the catalysts increases both the extent of dehydrogenation of cyclohexane into benzene, and the extent of isomerization of cyclohexane into methylcyclopentane. The rhenium sulfide-alumina catalysts have been found to be more active in producing dehydrogenation of cyclohexane than the rhenium-alumina catalysts with the same content of rhenium studied earlier [2].

In the course of this study a method of photometric determination of rhenium in the catalysts has been developed.

EXPERIMENTAL

The catalysts were prepared by impregnating commercial aluminum oxide with rhenic acid as described earlier [1]. Treatment of all the catalysts with hydrogen sulfide was performed in the following way: Purified hydrogen sulfide [3] from Kipp's apparatus was passed into a burette of 500 ml capacity, filled with water and a layer of vaseline. The catalyst was heated to 120° in a flow system in a gentle current of nitrogen, after which hydrogen sulfide was circulated through the system at the same temperature for a period of 3-4 hours, by means of a circulation pump. The quantity of hydrogen sulfide absorbed by the catalyst shows that the rhenium combines with sulfur in molar ratio 1:3.5. It may therefore be assumed that the compound obtained corresponds to the formula Re_2S_7.

The experiments to determine the catalytic properties of the rhenium sulfide-alumina catalysts were conducted in a flow apparatus using hydrogen under pressure, with a more accurate control of the rate of hydrocarbon supply than that described earlier [4]. The cyclohexane was displaced from a steel cylinder (dropping tube) by means of a piston, a constant rate of supply being secured by means of a Uorrena SD-2 motor. The hydrocarbon was passed over the catalyst for one hour (pre-experimental period), and then the experiment itself was continued for 5-6 hours.

Analysis of the cyclohexane catalyzates was conducted in a gas-liquid chromatography apparatus, with the following changes from that described earlier [2,5]: a detector was used for thermal conductivity, the sorbent was diatomite, the developing liquids were dicresylphosphate and dioctylphthalate, and the consumption of hydrocarbons in relation to hydrogen [6] was determined in nitrogen as gas-carrier. The apparatus also permitted of the separation of gaseous hydrocarbons in the range C_1–C_5. By means of these refinements it was possible to conduct the analysis with an accuracty of ± 1.2%. Separation was conducted on a column of length 6 m at 70°, with a rate of movement

of the gas-carrier equal to 30 ml per minute. The volume of sample did not exceed 0.01 ml. In order to check the separating power of the apparatus, chromatographic separation was performed on a synthetic mixture containing n-pentane, isopentane, 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane, cyclopentane, methylcyclopentane, cyclohexane, benzene, methylcyclohexane, n-heptane, and toluene. All these hydrocarbons were well separated, except 2,3-dimethylbutane from 2-methylpentane and 3-methylpentane from cyclopentane. The content of each component in the mixture was calculated on the basis of the area of the corresponding peak on the yield-curve in comparison with the total area of the curve, using coefficients corresponding to the number of hydrogen atoms in the hydrocarbon molecule. The gaseous catalysis products of composition between C_1 and C_4 were separated on alumina at various temperatures, while hydrogen and methane were separated at room temperature on carbon of type BAU. The individual details of the apparatus have been described earlier [7].

Control of the rhenium content in the rhenium sulfide-alumina catalysts was performed by means of a photometric method worked out for rhenium determination. The method has been fully described in connection with the determination of rhenium in rhenium-alumina [8]. In contrast with the earlier method, the rhenium was not now extracted simply with nitric acid, but with a mixture of nitric acid and hydrogen peroxide. The method was employed both for freshly prepared and for used catalyst samples.

TABLE 1. Results of Determining the Rhenium Content in Rhenium Sulfide-Alumina Catalysts by the Photometric Method

Rhenium content in initial catalysts, %	Optical density	Found		Rhenium content in initial catalysts, %	Optical density	Found	
		Rhenium, mg per g.	Percentage retained by catalyst, %			Rhenium, mg, per g.	Percentage retained by catalyst, %
	Before catalysis				After catalysis		
1.0	1.180	10	1	1.0	0.165	9	0.9
5.0	0.555	50	5	5.0	0.525	43	4.3
10.0	0.695	90	9	10.0	0.695	90	9.0
15.0	0.795	150	15	15.0	0.785	145	14.5

Blank solutions were prepared containing rhenium in quantities of 0.01 and 0.02 mg/ml and then, in intervals of 0.02 up to 0.20 mg/ml. For this purpose a weighted sample of 0.5000 g rhenium was placed in a glass beaker and treated with a mixture of 3 ml 13% nitric acid (density 1.072) and 3 ml hydrogen peroxide (density 1.10) while heating on a boiling water bath for 30 minutes. The contents were then transferred to a 50 ml measuring flask, made up to the mark with distilled water and shaken. The solution obtained thus contained 10 mg rhenium per 1 ml. The blank solutions were prepared from this by the method described earlier [8]. After one hour the optical density of the prepared blank solutions was determined relative to distilled water in cells with working surfaces 10 mm apart, by means of the photometer FEK-M, using a blue light filter. The determination of rhenium content in the catalyst was performed in the following way. 1.00 g of a sample of the catalyst previously ground to powder was placed in a glass beaker and treated with 3 ml of 13% nitric acid (density 1.072) and 3 ml of hydrogen peroxide (density 1.10), heating on a water bath for 30 minutes. The contents were transferred into a 50 ml measuring flask and made up to the mark with distilled water. 5 ml of this solution were filtered through a sintered glass filter number 3, and the solution collected in a 50 ml measuring flask to which was added 10 ml concentrated hydrochloric acid, 10 ml of 5% thiourea solution and 2 ml 20% stannous chloride in concentrated hydrochloric acid. The solution was then made up to the mark with distilled water. Photometric measurement was carried out after one hour, and the rhenium content determined by means of the calibration curve. The rhenium content in the catalyst was calculated according to the formula given in our previous work [8]. Table 1 gives the results of determining the rhenium content in rhenium sulfide-alumina catalysts before and after use in cyclohexane catalysis.

The results obtained indicate satisfactory concordance of the analytical results, and so confirm the suitability of the method described.

For catalysis a sample of cyclohexane was chosen characterized by the values: $n_D^{20} = 1.4262$ and $d_4^{20} = 0.7781$. The results, obtained with this and with the catalysts named, are shown in Table 2. It follows from the data here presented that increase in the quantity of rhenium from 1 to 15% in the catalysts causes the quantity of benzene produced in the catalyzates from cyclohexane to increase from 2.9 to 34.6%. The 1% rhenium sulfide-alumina catalyst

possesses only slight dehydrogenating (benzene content 2.9%) and isomerizing (methylcyclopentane content 5.1%) properties. Increase in the rhenium content of the catalyst from 1 to 5% produces a 7-fold increase in the dehydrogenating activity, and a 3-fold increase in the isomerizing activity. Side by side with these processes, a hydrogenolysis of the 5 membered cyclanes produced is observed. The 6.7% of these produced is converted into alkanes of the C_6 series: 2-methylpentane (2%); n-hexane (2.2%); and a mixture of 3-methylpentane and cyclopentane (2.5%). The hydrogenation-cracking is small during this process, and amounts only to 0.5% in all. We have observed these reactions earlier [1] in the case of the conversion of methylcyclopentane and n-hexane on a 20% rhenium sulfide-alumina catalyst under similar conditions.

TABLE 2. Properties of Cyclohexane Catalyzates obtained on Rhenium Sulfide-Alumina Catalysts. 500° 5 atm hydrogen, v = 1.0 HR^{-1}, and H_2 : HC = 5 : 1

Properties of catalyzate	Content of rhenium in catalyst, %			
	1	5	10	15
Refractive index, n_D^{20}	1.4300	1.4345	1.4370	1.4400
Density, d_4^{20}	0.7806	0.7834	0.7845	0.7875
Composition, weight %:				
ethane	—	Traces	Traces	0.2
propane	—	"	0.2	0.6
isobutane	—	0.3	0.2	0.6
n-butane	—	—	—	—
isopentane	—	~0.1	0.5	1.4
n-pentane	—	~0.1	0.3	0.6
2,2-dimethylbutane	—	Traces	Traces	0.2
2-methylpentane	—	2.0	3.3	5.8
mixture of 3 methyl-pentane and cyclopentane	—	2.5	2.7	4.5
n-hexane	—	2.2	2.1	4.2
methylcyclopentane	5.1	16.3	11.4	11.2
cyclohexane	92.0	56.3	47.8	35.9
benzene	2.9	20.2	31.4	34.6

Further increase in the rhenium content from 5 to 15% leads to a considerable increase in the benzene content (from 20.2 to 34.6%) and a small reduction in the methylcyclopentane content (from 16.3 to 11.2%) in the catalyzates. It should be observed that the 10% and 15% catalysts possess similar aromatizing and isomerizing capacities, but in the presence of the 15% catalyst a greater hydrogenation-cracking and hydrogenolysis are observed. Of the hydrogenolysis products (14.7%) in the presence of this catalyst, the following are observed in appreciable quantities: 2-methylpentane (58%); a mixture of 3-methylpentane and cyclopentane (4.5%) and n-hexane (4.2%). The products of hydrogenation cracking include: ethane (0.2%); propane (0.6%); isobutane (0.6%); isopentane (1,6%); and n-pentane (0.6%). It can be seen from these data that in the presence of this catalyst the conversion of cyclohexane occurs to the greatest extent, and that under these conditions the ratios of the dehydrogenation-cracking, isomerization, hydrogenolysis and hydrogenation-cracking amount to 10 : 3 : 4 : 1.

Thus, the rhenium sulfide-alumina catalysts containing rhenium in quantities of 5, 10, and 15%, possess not only dehydrogenation, but also isomerizing properties. Rhenium-alumina catalysts, investigated earlier under the same conditions for cyclohexane [2], possess only cracking properties.

SUMMARY

1. The catalytic properties of four rhenium sulfide-alumina catalysts have been investigated, with rhenium contents of 1, 5, 10, and 15%, for the conversion of cyclohexane at 500° and 5 atm hydrogen pressure in a flow-system.

2. All the catalysts investigated produce dehydrogenation of cyclohexane into benzene and its isomerization into methylcyclopentane. The extent of these reactions depends on the rhenium content in the catalysts.

3. A method has been worked out for determining rhenium in the catalyzates investigated, using the photometric method.

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THE PARTIAL ESTERIFICATION OF SOME AMINO ACIDS AND GLUTATHIONE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1677-1680, September, 1961
Original article submitted December 20, 1960

In the study of the structure of natural compounds there is ofter need to establish how many of various functional groups the molecule under investigation possesses. This problem can be solved by the use of the method of partial substitution. Up to now this method has chiefly been used in the chemistry of antibiotics for determination of the number of free amino groups and the molecular weight [1-3]. In order to use this method for determination of the number of free carboxyl groups, we have studied the partial esterification of some amino acids and their derivatives, and also the natural peptide, glutathione.

Incomplete esterification of polybasic amino acids leads to the formation of a complex mixture of products whose composition depends on the number of carboxyl groups in the starting compound. Thus, on esterification of dicarboxylic acids there are formed mono and diesters; in the case of tribasic acids it is possible to form triesters, etc. It is evident that the number of different esters formed in an incomplete esterification corresponds to the number of carboxyl groups in the molecule of the compound being studied (this is correct if we consider only the esters which differ in number but not in position of the ester groups). To establish the number of carboxyl groups it is important to choose such conditions of esterification as will assure obtaining all possible esters and to find a reliable process for separating the partly esterified derivatives.

We carried out the partial esterification using the method which is usually employed for obtaining esters of amino acids and peptides, the action of excess methanol in the presence of hydrogen chloride. The depth of the esterification was regulated by changing three factors: concentration of the alcoholic solution of HCl, temperature, and duration of the reaction. Separation of the resulting mixture of substances was carried out by paper electrophoresis. At pH more than five, the carboxyl groups of the amino acids are practically completely dissociated and carry a negative charge so that the conversion of any of them into an ester deprives the molecule of one ionizing group and decreases its charge by one. This produces a stepwise change in its electrophoretic mobility. Thus, by choosing a corresponding pH we can carry out an electrophoresis of all the products of partial esterification. In some cases there also occurs separation of isomeric esters, for example, α- and γ-methyl esters of glutamic acid. Since at a definite number of carboxyl groups such a separation is not desirable, the electrophoresis should be carried out at a pH sufficiently high to avoid showing a difference in degree of dissociation of the carboxyl groups.

Electrophoretic analysis of the products of partial esterification of glutamic acid, as would be expected, showed the presence of the starting acid, mono-, and diesters. The formation of the monoester occurs comparatively easily; it is obtained in large amounts by treatment of glutamic acid with 0.1 N HCl in methanol at 0 and 20°. The diester here is almost not formed and to obtain it, it is necessary to use considerably more severe conditions (boiling with 0.1 N HCl/CH_3OH, keeping 48 hours with 1 N HCl/CH_3OH, etc.). Such a sharp difference is related to the fact that the γ-carboxyl of glutamic acid is esterified much more easily than is the α-carboxyl group. The decreased activity of the latter is evidently explained by the ammonization of the amino group in the α-position. Actually, on the electrophoretogram we do not find the spot for the α-methyl ester of glutamic acid. Esterification of 2,4-dinitrophenylglutamic acid whose amino group lacks basic properties, goes much more easily.

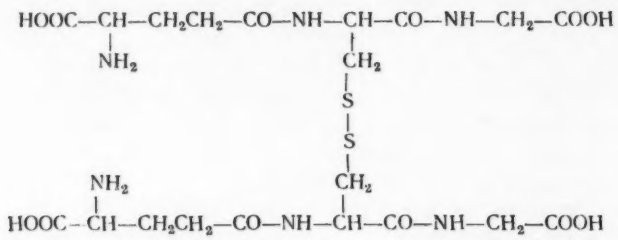
In this case there is marked formation of the diester even after three hours action of 0.1 N HCl/CH_3OH at 20°. The inhibiting effect of the amino group on the esterification is considerably weakened in β-alanine, where it is removed from the carboxyl group by two carbon atoms. On the other hand, this effect is clearly shown in the esterification on the α-amino acids, especially in glycine, leucine, threonine, and lysine. The formation of the methyl esters of these amino acids in 0.1 N HCl/CH_3OH goes very slowly, so that for esterification we must use 1 N HCl/CH_3OH. Partial esterification of aspartic acid occurs in the same way as for glutamic acid. Cystine has two carboxyl

groups and both are in the α-position to the amino group. Corresponding to the suggestion above, esterification of cystine requires the use of relatively sever conditions: treatment with 1 N HCl/CH_3OH for 48 hours.

The behavior of the peptide glycyl-leucine under conditions of partial esterification recalls the behavior of β-alanine. Thus, even on treatment with 0.1 N HCl/CH_3OH much ester is formed. Our result agrees with the data in the literature on complete esterification of peptides and proteins. Esterification by methanol in the presence of HCl is the usual method for chemical modification of proteins and higher peptides and goes well under mild conditions [4,5]. This is explained by the fact that under such conditions we almost never encounter carboxyl groups in the α-position to free amino groups, since this is possible only in the formation of β- and γ-peptide bonds which are not present in natural proteins.

The separation of the mixture of products from partial esterification in all these cases is carried out by paper electrophoresis at pH 4.3-5.6. For the dinitrophenyl derivative, however, we used a buffer with pH 8.3, which contained 50% acetone.

In order to explain the possibility of using the method for peptides we carried out the partial esterification of glutathione. Oxidized glutathione



has four carboxyl groups; two of these occur in the α-position to a free amino group. On the basis of the results obtained in the esterification of the amino acids we would expect that they would be esterified with more difficulty than the other two. This was confirmed in the experiment. Even after three hours esterification with 0.01 N HCl/CH_3OH there was formation of a considerable amount of mono- and diesters of glutathione (Table 1). For the formation of tri- and tetraesters of glutathione it was necessary to use 48 hour esterification in 0.1 N HCl/CH_3OH. Thus, although esterification of glutathione occurs with comparative difficulty, we were able to find conditions which assured obtaining products of all degrees of substitution. The separation of the resulting mixture of reaction products was carried out by electrophoresis at pH 4.3 and 5.8. At pH 4.3 we find separation of isomeric esters of glutathione (Table 2). This is explained by the fact that in a weak acid medium the carboxyl group radicals of glutamic acid are dissociated to a greater extent than the glycine carboxyls (in the scheme and in the tables they are called α- and ω-COOH, respectively). This difference which depends on the effect of the amino groups, is leveled out at pH 5.8, so that the behavior in electrophoresis in this medium is more satisfactory. We should note the good agreement between the values for effective charge of the different glutathione esters calculated by the formula

$$pH - pK' = \lg \frac{[A^-]}{[HA]}$$

and their mobilities in paper electrophoresis at pH 4.3 and 5.8.

Partial esterification of glutathione showed that this method for determining the number of free carboxyl groups can be applied to peptides. We can assume that partial esterification followed by electrophoretic separation of the reaction products will find use in the chemical modification of the peptides.

EXPERIMENTAL

Method of partial esterification. Five mg of amino acid or peptide in a tube with a ground glass stopper were treated with 1 ml of a solution of hydrochloric acid in absolute methanol. The mixture remained at room temperature or in a refrigerator at 0°. The solution was evaporated in a vacuum at room temperature, and the dry residue was treated with absolute methanol and repeatedly evaporated in a vacuum. The dry residue was dissolved in a buffer mixture and this solution was deposited on the electrophoretogram.

Paper electrophoresis was carried out in a pyridine-acetate buffer mixture at a voltage of 400-1000 V. The electrophoretogram was developed with a solution of ninhydrin in acetone. The intensity of the spots was estimated visually.

SUMMARY

1. We have studied the partial esterification of some amino acids and peptides.

TABLE 1. Partial Esterification of Oxidized Glutathione

Reaction products*	Esterification conditions						
	0.01 N HCl/CH_3OH		0.0 N HCl/CH_3OH			1 N HCl/CH_3OH	
	3 hours	21 hours	1 hr	21 hr	48 hr	48 hours	70 hours
Glutathione	+	+	+	+	+		
Glutathione monoester	+	+	+	+	+	+	
Glutathione diester	+	+	+	+	+	+	+
Glutathione triester			+	+	+	+	+
Glutathione tetraester					+	+	+

* The sign + shows that this substance was found in the electrophoretic analysis of the mixture obtained under the conditions given.

TABLE 2. Electrophoretic Separation of Products of the Esterification of Oxidized Glutathione

Substance	pH 4.3		pH 5.8	
	Effective charge	Distance traveled, cm*	Effective charge	Distance traveled
Glutathione	-1.68	-8	-2	-7.4
α-Monoester of glutathione	-0.68	-3.3	-1	-3.7
ω-Monoester of glutathione	-0.84	-4.3	-1	-3.7
α,ω-Diester of glutathione	-0.16	-0.7	0	0
ω,ω-Diester of glutathione	0	0	0	0
α,ω,ω-Triester of glutathione	+1	+4	+1	+4
Tetraester of glutathione	+2	+8.5	+2	+8.1

* The sign - shows shift of the substance to the anode; +, to the cathode. Electrophoresis carried out at 1000 V, duration three hours.

2. Partial esterification in conjunction with electrophoresis for separation of the reaction products can be used as a method for determining the number of carboxyl groups.

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THE PREPARATION AND PROPERTIES OF CARBOXYALKYLENE DERIVATIVES OF CITRACONIC ACID IMIDE

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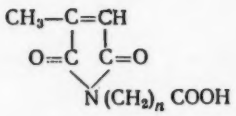
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1680-1685, September, 1961
Original article submitted December 24, 1960

We have previously described the synthesis of N-alkylimides of citraconic acid [1,2]. These imides are of interest as monomers which permit formation of polymers and copolymers with heterocycles in the chain.

In the present study we wished to synthesize derivatives of citraconic acid imide which contained reactive groups substituted on the nitrogen. Such derivatives could give polymers and copolymers with new properties and would permit carrying out reactions in the macrochain including the creation of branched polymers. It seemed to be of the greatest interest to introduce a carboxyl group, that is, to obtain and study the properties and polymerization of citraconyl amino acids



Citraconyl-β-alanine also is of very great interest since it is an isomer of hematinic acid, a product of the oxidative splitting of hemoglobin.

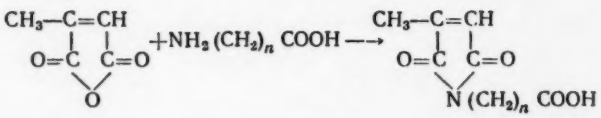
There is no information in the literature on the preparation of citraconyl amino acids, but work is known on the synthesis of imides of phthalic and succinic acids, on whose nitrogen there are methylene carboxyl groups, CH_2COOH. In 1883 Drechsel [3] isolated phthalyl glycine by fusing glycine with phthalic anhydride

$$NH_2CH_2COOH + C_6H_4(CO)_2O \rightarrow C_6H_4(CO)_2NCH_2COOH$$

with almost theoretical yields; m.p. 191-192°. The author showed the possibility of wide use of this reaction. Radenhausen [4] prepared esters of phthalyl glycine $C_6H_4(CO_2)_2NCH_2COOC_2H_5$ and succinyl glycine $C_2H_4(CO_2)_2NCH_2COOC_2H_5$ by heating a mixture of the calculated amounts of anhydride and ethyl glycinate on an oil bath.

EXPERIMENTAL

Synthesis of citraconyl glycine and citraconyl-β-alanine. Citraconyl glycine and citraconyl-β-alanine were prepared by condensation of the amino acid with citraconic anhydride by the scheme



n=1 or 2.

In order to establish the best method for condensation, we carried it out in solution (benzene, toluene, or water) or by fusing at various temperatures. At the end of heating, the solvent was distilled off in a vacuum and the resulting citraconyl glycine or citraconyl alanine was extracted from the reaction mixture with hot benzene. When the benzene was cooled, the citraconyl amino acid precipitated in the form of colorless crystals which were recrystallized from benzene.

A mixture of 22.4 g of citraconic anhydride (0.2 M) and 1 g of glycine (0.2 M) was heated in a Wurtz flask fitted with a thermometer, the mercury bulb of which dipped into the reaction mixture. The outlet tube of the flask was connected to a descending air condenser. Reaction temperature: 6 hours at 130-140°, 2 hours at 140-160°, 1.5 hours at 160-200°. We obtained 19.7 g (58%) of citraconyl glycine with m.p. 127-128°. Found: C 49.9; H 3.94; N 8.24%. $C_7H_7O_4N$. Calculated: C 49.7; H 4.14; N 8.29%.

A mixture of 11.2 g (0.1 M) of citraconic anhydride and 8.9 g (0.1 M) of β-alanine was heated in the same flask and with the same temperature regime. We obtained 6 g (33%) of citraconyl-β-alanine with m.p. 85-86°. Found: C 51.99; H 4.92; N 7.65%. $C_8H_9O_4N$. Calculated: C 52.46; H 4.92; N 7.28%.

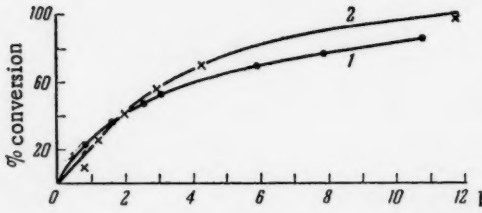


Fig. 1. Rate of conversion of amino acid (1, β-alanine; 2, glycine) into N-citraconyl amino acid in a melt at 80°.

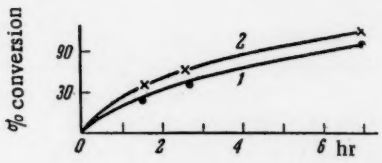


Fig. 2. Rate of conversion of amino acid (1, β-alanine; 2, glycine) into N-citraconyl amino acid in water solution at 100°.

A mixture of 11.2 g (0.1 M) of citraconic anhydride, 7.5 g (0.1 M) glycine, and 20 ml of water was boiled in a flask with a reflux condenser for six hours. We obtained 9.9 g (58.6%) of substance with m.p. 128-129°. It gave no melting point depression with the product of the first experiment.

A mixture of 5.6 g (0.05 M) of citraconic anhydride, 4.45 g (0.05 M) of β-alanine, and 10 ml of water was boiled in a flask with a reflux condenser for 6 hours. We obtained 5.7 g of citraconyl-β-alanine with m.p. 85-86° which gave no depression with the product of the second experiment. The reaction did not take place in benzene and toluene. Then the experiment was carried out at different temperatures and the course of the reaction was followed by the decrease in primary amino groups determined by the Van Slyke method. The results of the experiments are shown in the graphs of Figs.1 and 2.

As Figs.1 and 2 show, in a melt at 80° and water solution at 105° after 10 hours, the reaction takes place to the extent of 75-80%.

Synthesis of the chlorides of citraconyl glycine and citraconyl-β-alanine. The chlorides were obtained by the action on the acids of thionyl chloride in benzene solution.

In a three necked flask fitted with a dropping funnel, reflux condenser (with a calcium chloride tube), and a mechanical stirrer, was placed a suspension of 3.4 g of citraconyl glycine in 20 ml of dry benzene. In the dropping funnel we placed 3.35 g of thionyl chloride in 10 ml of benzene. Then, with stirring, the solution of thionyl chloride was added dropwise and when all the solution had been added, the mixture was left over night at room temperature, after which the benzene was distilled off, hydrogen chloride was neutralized with dry potassium carbonate, and the acid chloride was distilled twice in a vacuum at a pressure of 1 mm. We obtained 2.38 g of a crystalline product (63.2%) with m.p. 29-31°, b.p. 115-117° (1 mm), d_4^{30} 1.3207, n_D^{30} 1.5037; Found MR 48.28; Calculated MR 48.64.

Under the same conditions we obtained the acid chloride of citraconyl-β-alanine. For the reaction we took 10 g of citraconyl-β-alanine in 40 ml of benzene and 7.15 g of thionyl chloride in 10 ml of benzene. We obtained 7.55 g of acid chloride of citraconyl-β-alanine (about 64%) in the form of a viscous oil; b.p. 146-147° (4-5 mm), n_D^{20} 1.5120; d_4^{20} 1.3021; Found MR 46.43; Calculated MR 46.25.

Methyl esters of citraconyl glycine and citraconyl-β-alanine. A solution of 8.6 g of citraconyl glycine was boiled in 50 ml of methyl alcohol (containing 3% hydrogen chloride) in a 100 ml flask with a reflux condenser for six hours. Then, after neutralizing the hydrogen chloride, with anhydrous potash, the excess methyl alcohol was distilled off. The methyl ester of citraconyl glycine was extracted with ether, dried, and distilled in a vacuum. We obtained 5.15 g of a viscous oil (55.3%) with b.p. 125-127° (2.5 mm), d_4^{20} 1.2300; n_D^{20} 1.4878. Found: C 52.79; H 5.29; N 7.54%; MR 42.85. $C_8H_9O_3N$. Calculated: C 52.46; H 4.92; N 7.65%; MR 43.03.

In a 100 ml three necked round bottomed flask fitted with a dropping funnel, mechanical stirrer, and reflux condenser, we placed 50 ml of absolute methyl alcohol, and then added dropwise 8 g of citraconyl glycine chloride in 10 ml of benzene. When all the acid chloride had been added, the mixture remained overnight at room temperature and then was boiled under reflux for four hours after which the solvent was distilled off on a water bath. The methyl ester of citraconyl glycine was extracted with ether, the hydrogen chloride was neutralized with potassium carbonate, the extract was dried with sodium sulfate, and after distillation of the ether, was distilled in a vacuum. We obtained 4.5 g (57.7%) of ester with b.p. 125-127° (2.5 mm), n_D^{20} 1.4878; d_4^{20} 1.2300.

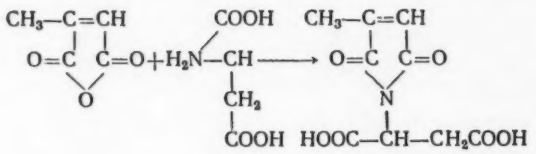
A mixture of 4.3 g of citraconyl-β-alanine and 20 ml of methyl alcohol (saturated with 2.5% hydrogen chloride) was boiled in a flask with a reflux condenser for six hours. We isolated 2.24 g of methyl ester of citraconyl-β-alanine (48.4%) with b.p. 147-148° (5-6 mm); d_4^{20} 1.2000; n_D^{20} 1.4895. Found: C 54.82, H 5.68; N 7.34; OCH_3 16.37%; MR 48.38. $C_9H_{11}O_3N$. Calculated: C 54.82; H 5.68; N 7.10; OCH_3 15.74%. MR 48.64.

In a 100 ml three necked round bottomed flask fitted with a dropping funnel, mechanical stirrer, and reflux condenser we placed 40 ml of absolute methyl alcohol and then added dropwise 6.45 g of citraconyl-alanine chloride in 10 ml of benzene. After all the acid chloride had been added, the mixture was left overnight at room temperature and then refluxed for four hours, after which the solvent was distilled off on a water bath. The methyl ester of citraconyl-β-alanine was extracted with ether, the hydrogen chloride was neutralized with potassium carbonate, the extract was dried with sodium sulfate and after distillation of the ether was distilled in a vacuum; b.p. 147-148° (5-6 mm), d_4^{20} 1.2000; n_D^{20} 1.4895.

Phenyl esters of citraconyl glycine and citraconyl-β-alanine. A mixture of 1.5 g of citraconyl glycine chloride, m.p. 129-131°; and 0.75 g of phenol, m.p. 41° was placed in a reaction flask. The reaction was carried out in the melt for 1.5-2 hours. The mixture became strongly colored. After cooling the mixture, it crystallized. After recrystallization from benzene we obtained 0.37 g (20%) of colorless crystals with m.p. 82-83°. Found: N 5.70%. $C_{13}H_{11}O_4N$. Calculated: N 5.71%.

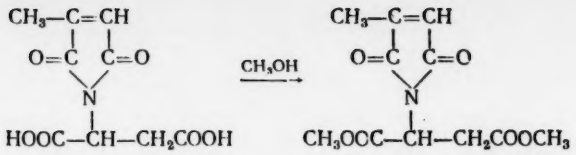
A mixture of 1.5 g of citraconyl-β-alanine chloride and 0.7 g of phenol in 18 ml of benzene was boiled for 2.5 hours in a flask under reflux. At the end of the reaction most of the benzene was distilled off and the crystals which precipitated from the mixture were filtered off and recrystallized from benzene; yield 0.53 g (30%); m.p. 80-81.5°. Found: C 64.67; H 5.17; N 5.56%. $C_{14}H_{13}O_4N$. Calculated: C 64.86; H 5.02; N 5.40%.

Citraconyl aminosuccinic acid. A mixture of aminosuccinic acid 6.65 g (0.05 M), citraconic anhydride 5.6 g (0.05 M), and 15 ml of water was placed in a round bottomed flask fitted with a thermometer, (the mercury bulb of which was placed in the reaction mixture) and a mechanical stirrer.



The reaction was carried out with stirring and heating on a glycerol bath. The initial reaction temperature was 112° which was gradually raised in the course of 12 hours as the water evaporated, to 130° and for the next 30 minutes was kept at 140°. After cooling, the mixture was poured into 150 ml of acetone. The unreacted aminosuccinic acid precipitated (2.65 g) and was filtered off. After cooling the filtrate with solid carbon dioxide we precipitate the citraconyl aminosuccinic acid. The melting point after recrystallization from acetone was 174-175.5°; yield 3.9 g (57%). The content of carboxyl groups in the citraconyl aminosuccinic acid was determined by titration with NaOH (0.0964 N). Found, carboxyl groups, 40.7%, calculated 39.8%. Found: C 47.96; H 4.30; N 6.01%. $C_9H_9O_6N$. Calculated: C 47.58; H 3.92; N 6.16%.

Dimethyl ester of citraconyl aminosuccinic acid. A mixture of 10.5 g (0.0465 M) of citraconyl aminosuccinic acid and 50 ml of methyl alcohol (1.2 M) (containing 3.5% hydrogen chloride) was boiled under reflux for six hours. After distillation of the methyl alcohol, the residue was recrystallized from acetone. We obtained 6.73 g of colorless crystals with m.p. 68.5-69.5°; yield 57%. Found: OCH_3 24.25; C 51.55; H 5.25; N 5.44%. $C_{11}H_{13}O_6N$. Calculated: OCH_3 24.32; C 51.76; H 5.1; N 5.49%.



DISCUSSION OF EXPERIMENTAL RESULTS

According to the experimental data, condensation of amino acids with citraconic anhydride occurs at temperatures of 80-105°, while the reaction of formation of alkylimides of maleic acid and alkylimides of citraconic acid occurs only at 140-200° [5]. Even in 1851 Gottlieb [6] obtained phenylcitraconic imide by boiling aniline with citraconic anhydride in water, and his experiment was repeated by us. Comparing all these results, we explained the ease of condensation of the amino acids and arylamines with anhydrides by the mobility of the hydrogen atom of the amino group.

The basicity constant of the amide has an indirect (inverse) relation with the mobility of the hydrogen atom of the amino group, since

$$K_{bas} = \frac{[RNH_3^+][OH^-]}{[RNH_2]},$$

which follows from the equation

$$RNH_2 + H_2O \rightleftarrows RNH_3^+ + OH^-$$

The equilibrium shift to the left side is determined by the ease of protonization, that is, the mobility of the hydrogen atom of the ammonium ion which depends on the shift of the density of the electron cloud to the electron acceptor substituent. This shift is the reason for the increased mobility of the hydrogen atoms in the amino groups which produces the great ease of condensation of amines with the anhydride. Therefore, amines which have a low basicity constant are condensed with anhydrides at lower temperature than amines with high basicity. We give a table of basicity constants of the amines

$CH_3NH_2 = 5,0 \cdot 10^{-4}$
$C_2H_5NH_2 = 5,6 \cdot 10^{-4}$
$p\text{-}C_3H_7NH_2 = 5,3 \cdot 10^{-4}$
$i\text{-}C_3H_7NH_2 = 4,7 \cdot 10^{-4}$

While

$C_6H_5NH_2 = 5,4 \cdot 10^{-10}$
$NH_2(CH_2)_2COOH = 6,4 \cdot 10^{-11}$
$NH_2CH_2COOH = 2,6 \cdot 10^{-12}$

SUMMARY

1. We have prepared and characterized the previously undescribed citraconyl aminoacetic acid, its chloride, and methyl and phenyl esters; citraconyl aminopropionic acid, its chloride, methyl and phenyl esters; citraconyl aminosuccinic acid and its dimethyl ester.

2. The ease of condensation if amino acids with citraconic anhydride is explained by the great mobility of the hydrogen atoms of the amino groups.

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THE SYNTHESIS AND REACTIONS OF NEW VINYL ESTERS

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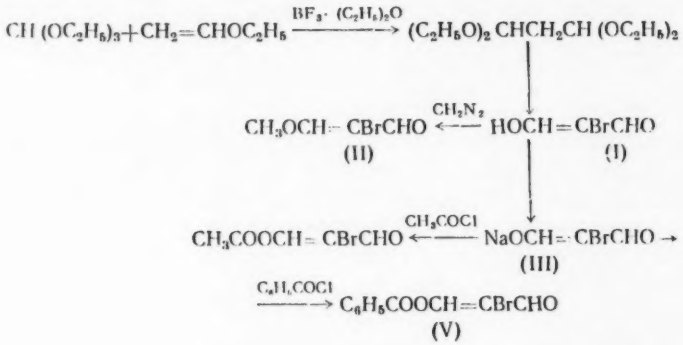
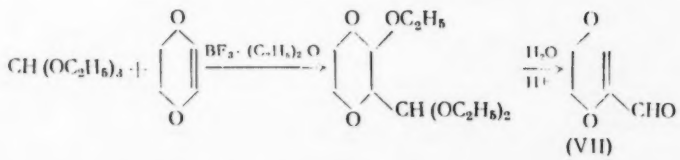
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1685-1688, September, 1961
Original article submitted March 10, 1961

In studying in our laboratory the methods of synthesis of new vinyl esters, we have obtained some ester of 3-hydroxyacrolein. As is known, acrolein easily undergoes the diene condensation with vinylethers [1-4]. It seemed interesting to see whether ethers and esters of 3-hydroxyacrolein would undergo the diene condensation. We obtained the latter by the following scheme:



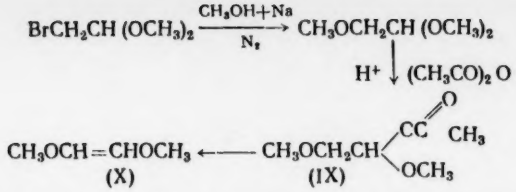
2-Bromo-3-hydroxyacrolein (bromomalonic aldehyde) (I), prepared according to [5-7] was converted by treatment with diazomethane into the methyl ether (II) and by the action of acetyl chloride on the sodium salt (III) we formed the acetate (IV); the same process gave the benzoate (V). These ethers and esters (II), (IV), and (V) were very easily hydrolyzed by water and moist air, and when kept, easily condensed.

The diene condensation of (II), (IV), and (V) with vinylbutyl ester was not successful, since the reaction product completely resinified, probably because of the hydrogen bromide which was evolved at high temperature. Therefore, we decided to study the condensation of ethyl orthoformate with dioxene [8] in order to convert the resulting reaction product into 2-formyl-p-dioxene (VII) which is also a substituted acrolein. It was shown that the reaction occurs smoothly in the presence of boron trifluoride etherate:



Here there is formed 2-ethoxy-3-diethoxymethyl-p-dioxane (VI) which is converted by saponification into 2-formyl-p-dioxene (VII). The resulting unsaturated aldehyde (VII) is very hygroscopic and was usually isolated as the hydrate. The cyclic structure which we ascribed to aldehyde (VII) was confirmed by the absence of a reaction with ferric chloride, by the results of elementary analysis, and also from spectroscopic data (presence of frequencies in the Raman spectrum characteristic for the bond groups $-C=C-C=O$).

We also studied a method for preparing 1,2-dimethoxyethylene (X) which we obtained as follows:



1,1,2-Trimethoxyethane, obtained from the acetal of bromoacetaldehyde [9] by boiling with acetic anhydride in the presence of a trace of p-toluenesulfonic acid, was converted into the acylal (IX) which by slow distillation was transformed into 1,2-dimethoxyethylene (X). However, the yield of (X) did not exceed 20%. The resulting dimethoxyethylene (X) was a mixture of isomers in the ratio 3.5:1, the study of which will be continued.

EXPERIMENTAL

2-Bromo-3-methoxyacrolein (II). To an ether solution of diazomethane obtained from 5 g of nitrosomethylurea was added gradually 5 g of bromomalonic aldehyde (I) and after one hour the ether was distilled off and the residue recrystallized from a mixture of ligroin and ether. We thus obtained 4.46 g (81.6%) of 2-bromo-3-methoxyacrolein (II) with m.p. 56-57°. Found: C 29.24; 29.11; H 3.46; 3.36; Br 48.24; 48.30%. $C_4H_5O_2Br$. Calculated: C 29.1; H 3.05; Br 48.46%.

2-Bromo-3-acetoxyacrolein (IV). A water solution of 6.04 g of bromomalonic aldehyde (I) was neutralized with 1 N sodium carbonate solution to a neutral reaction to phenolphthalein (40 ml). The solution was evaporated in a vacuum of 50 mm at a bath temperature of 35-45°, to dryness. The residue was washed with acetone and the sodium salt (III) which separated was filtered off and dried in a desiccator over sulfuric acid. In all we obtained 6.02 g (87%) of the sodium salt of bromomalonic aldehyde (III) [10]. To 1 g of this salt and 25 ml of ether we added with stirring in the course of 5 minutes and dropwise 0.45 g of acetyl chloride; stirring was continued for 15 minutes more, after which the reaction mixture was filtered and the filtrate was evaporated. We thus obtained 0.71 g (67.3%) of 2-bromo-3-acetoxyacrolein (IV) with m.p. 72-74° (after recrystallization from a mixture of ligroin and ether). Found: C 29.62; 29.71; H 2.92; 3.02; Br 43.64; 43.48%. $C_5H_5O_3Br$. Calculated: C 31.1; H 2.61; Br 41.43%.

2-Bromo-3-benzoxyacrolein (V). To 1 g of sodium salt of bromomalonic aldehyde obtained by the method described above and 30 ml of ether we added 0.71 g of benzoyl chloride with stirring in the course of 5 minutes. Stirring was continued for another six hours after which the solid was filtered and the filtrate was evaporated. The residue after recrystallization from a mixture of ligroin and ether had a m.p. 100-102°. We thus obtained 1.05 g (81.6%) of 2-bromo-3-benzoxyacrolein (V). Found: C 47.21; 47.16; H 3.09; 3.06; Br 30.69; 30.7%. $C_{10}H_7O_3Br$. Calculated: C 47.01; H 2.75; Br 31.33%.

2-Ethoxy-3-diethoxymethyl-p-dioxane (VI). To 15 g (0.1 M) of ethyl orthoformate and 0.1 g of boron trifluoride etherate we added dropwise 9 g (0.1 M) of dioxene with stirring at a temperature of 40-45°. Addition lasted 20 minutes, after which the mixture was stirred for 1 hour more at the same temperature. To the reaction mixture we added 2 g of finely ground sodium bicarbonate, and stirring was continued for three hours at 25°, after which the residue was filtered off and the filtrate was distilled in a vacuum. We thus isolated 8.5 g of orthoformic ester with b.p. 46-47° (16 mm) and 8 g (77.8%) of 2-ethoxy-3-diethoxymethyl-p-dioxane (VI) with b.p. 135-137° (20 mm); n_D^{20} 1.4337. Found: C 56.14; 56.0; H 9.37; 9.29%. $C_{11}H_{22}O_5$. Calculated: C 56.38; H 9.46%.

2-Formyl-p-dioxene (VII). A mixture of 4.68 g (0.02 M) of 2-ethoxy-3-diethoxymethyl-p-dioxane (VI) and 15 ml of 2% hydrochloric acid was boiled in a distilling flask; alcohol distilled off and the mixture became homogeneous. The water solution was neutralized with 1 g of sodium bicarbonate and extracted ten times with 15 ml of ether. The ether extract was dried with magnesium sulfate, the ether was removed, and the residue was distilled in a vacuum. We thus obtained 1.13 g (49.6%) of 2-formyl-p-dioxene (VII) with b.p. 216-217° (12 mm). The distilled product crystallized in the receiver and after recrystallization from a mixture of ether and ligroin had m.p. 40-42°. Found: C 52.12; 52.19; H 5.49; 5.3%. $C_5H_6O_3$. Calculated: C 52.63; H 5.3%.

The combination scattering spectrum in dioxane had the following frequencies: 1695, 1635, 1470, 578, 418 cm^{-1}. The lines 1695, 1635 are characteristic for the grouping of atoms $-C=C-C=O$. The substance did not give a color with an alcoholic solution of ferric chloride. The red 2,4-dinitrophenylhydrazone melted at 236-237°.

1,1,2-Trimethoxyethane (VIII) [11]. We dissolved 115 g of metallic sodium in 2.1 liters of methanol and added 710 g of the acetal of bromoacetaldehyde with stirring at 25°. The reaction product was boiled for 24 hours

under reflux in a stream of nitrogen, after which the sodium bromide which separated was filtered off (347 g) and the reaction product was distilled in a column with 20 theoretical plates. After removal of the alcohol, we thus separated 236 g (46.8%) of 1,1,2-trimethoxyethane (VIII) with b.p. 125-126° (741 mm), n_D^{25} 1.3930. The literature [12] gives b.p. 126-127.5°, n_D^{25} 1.3901.

1,2-Dimethoxy-1-acetoxyethane (IX). A mixture of 36 g (0.3 M) of 1,1,2-trimethoxyethane (VIII), 31 g (0.3 M) of acetic anhydride, and 0.5 g of para-toluenesulfonic acid was slowly heated so that the methyl acetate which formed distilled as it was formed (during the reaction 19 ml of methyl acetate distilled off) (b.p. 55-58°). After cooling, the reaction product was distilled in a vacuum and we obtained 12.84 g of 1,1,2-trimethoxyethane with b.p. 32-34° (15 mm), and 20.9 g (73.1%) of 1,2-dimethoxy-1-acetoxyethane (IX) with b.p. 64-65° (14 mm), n_D^{25} 1.4055. Found: C 48.58; 48.72; H 8.28; 7.97%. $C_6H_{12}O_4$. Calculated: C 48.64; H 8.16%.

A mixture of 36 g (0.3 M) of 1,1,2-trimethoxyethane (VIII), 80 g (0.78 M) of acetic anhydride, and 1 drop of concentrated sulfuric acid stood for 14 hours at room temperature and then the reaction mixture was poured into 300 ml of ice water and extracted with carbon tetrachloride. The extract was washed twice with a saturated solution of sodium bicarbonate, dried with calcium chloride, and distilled in a vacuum. We thus obtained 19.2 g (43.2%) of 1, 2-dimethoxy-1-acetoxyethane (XI) with b.p. 62-64° (12 mm), n_D^{22} 1.4055.

1,2-Dimethoxyethylene (X). We boiled 26 g of 1,2-dimethoxy-1-acetoxyethane (XI) for two hours in a flask with a reflux condenser at 162-165°, after which the resulting mixture of methyl alcohol and dimethoxyethylene was slowly distilled from a Favorskii flask. We thus obtained 20 g of a mixture with b.p. 71-145°. The reaction product was washed with a concentrated soda solution, dried over potash, and distilled from a column with 20 theoretical plates. We thus obtained 2.2 g of 1,2-dimethoxyethylene (X) with b.p. 97-99°, n_D^{22} 1.4184, and 0.61 g of 1,2-dimethoxyethylene (X) with b.p. 103°, $n_D^{20.5}$ 1.4204. The literature [13-14] gives b.p. 97-99°; 102°, n_D^{25} 1.4190.

SUMMARY

1. We have obtained for the first time ethers and esters of 2-bromo-3-hydroxyacrolein.

2. Orthoformic ester condenses with dioxene and the condensation product is easily converted to 2-formyl-p-dioxene.

3. The acylal obtained from 1,1,2-trimethoxyethane gives on pyrolysis 1,2-dimethoxyethylene.

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THE PROBELEM OF DETERMINATION OF THE DIRECTION OF THE MESOMERIC EFFECT OF SUBSTITUENTS BY THE SUTTON RULE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1688-1691, September, 1961
Original article submitted December 13, 1960

The direction of the mesomeric effect (π-effect) of substituents in the aromatic nucleus can be determined by the Sutton rule [1], recommended by Ingold [2,3] by comparison of the dipole moments of the molecules C_6H_5X and CH_3X (or $(CH_3)_3CX$) which have the same substituent, X.* Sutton found that independent of the direction of the individual moments the difference in dipole moments C_6H_5X and CH_3X (or $(CH_3)_3CX$) as a rule always corresponded to the direction of the mesomeric effect in aromatic compounds. This regularity could be interpreted in orienting fashion as follows. The size and direction of the moment of the bond C—X (μ_σ) in the molecule CH_3X is basically determined by the shift of the valence pair of σ-electrons to the atom C or X and the distance between them. It depends on the relative electronegativity of both atoms and can be connected with the inductive (I) effect (σ-effect) of substituent X. In the molecule of C_6H_5X the moment μ_σ is combined with the moment μ_M, produced by the mesomeric shift of the π-electrons from the benzene ring to substituent X (-M effect) or from X to the ring (+M effect). If we assume that the moment μ_σ in the molecules C_6H_5X and CH_3X is the same, and that the moment of the bond C—H in the group C_6H_5X (in the para-position) and CH_3 does not differ in them (all this is true only as a first approximation), then $\mu(C_6H_5X) = \mu_\sigma + \mu_M$. When the vectors μ_σ and μ_M agree in direction, then the absolute value of the dipole moment of C_6H_5X will be greater than in CH_3X.

In the opposite case, the moment of C_6H_5X will be less than the moment of CH_3X. Therefore, a negative value of the algebraic difference** $\mu(C_6H_5X) - \mu(CH_3X) = \mu_M$ shows a -M effect of substituent X, and a positive value shows a +M effect.

The Sutton rule not only does not give a quantitative estimate of the M effect, but is far from being always correct. Thus, for example, for $C_6H_5C(CH_3)_3$ it leads to $\mu_M = 0.42D$ (see table), although the group $C(CH_3)_3$ in general does not have a mesomeric effect. In the case of $C_6H_5Si(CH_3)_3$ $\mu_M = +0.44D$, while the group $Si(CH_3)_3$ can only acquire π-electrons because of $p_\pi - d_\pi$ bonding with the benzene ring (- M effect), but cannot give them up at all. The difference in dipole moments of C_6H_5NC and CH_3NC is positive although the isonitrile group has a -M effect. The value of μ_M for toluene (+0.37D), corresponding in sign to σ, π-conjugation of the methyl group with the aromatic nucleus (+M effect), cannot be so high.

All these variations from the Sutton rule led us to seek an explanation so as to define the limits of its use. We have found that it is actually the algebraic difference of the dipole moments of the molecules C_6H_5X and CH_3X - μ_M. According to the rule of vector additivity of the dipole moments of the tetrahedral molecule CH_3X (X is a regular substituent) we can state

$$\mu(CH_3X) = \mu(C—X) - 3\mu(C—H)\cos 70° = \mu(C—X) - \mu(C—H). \quad (1)$$

The dipole moment of C_6H_5X is expressed as the vector sum of four colinear moments:

$$\mu(C_6H_5X) = \mu(C—X) - \mu(C_{ar} — H) + \mu_\pi + \mu_i, \quad (2)$$

* Instead of monosubstituted benzene, disubstituted benzenes can be used for this purpose, and also the corresponding mono- or disubstituted acetylenes.

** Algebraic subtraction is permissible only in the case of a regular substituent the direction of whose dipole does not agree with the direction of the valence bond of X with CH_3 or C_6H_5, we should use vector subtraction.

where $\mu(C_{ar}-H)$ is the moment of the bond C−H in the para-position to the substituent X, μ_π is the moment depending on the reaction of the π-cloud of the benzene ring with the π-electrons or vacant orbits of the substituent X (± M effect), and μ_i is the moment which is induced in the benzene ring when the substituent X enters it. μ_M is the difference of (1) and (2)

$$\mu_M = \mu(C_6H_5X) - \mu(CH_3X) = \mu(C_{al}-H) - \mu(C_{ar}-H) + \mu_\pi + \mu_i = \Delta_H + \mu_\pi + \mu_i. \quad (3)$$

It is then assumed that $\mu(C-X)$ in CH_3X and C_6H_5X is the same, although in some cases this is true only as a first approximation.

Thus, we see that the value of μ_M is not at all identical with μ_π, and differs from the π-moment by $\Delta_H + \mu_i$, where $\Delta_H = \mu(C_{al}-H) - \mu(C_{ar}-H)$* is constant. This is why the Sutton rule indicates the presence of a +M effect in the group $C(CH_3)_3$ while actually $\mu_M = \Delta_H + \mu_i (\mu_\pi = 0)$. This also explains the abnormally great value of μ_M in toluene, which has $\mu_\pi \ll \mu_M$, since $\mu_\pi = \mu_M - \Delta_H - \mu_i$. On replacement of CH_3X by $(CH_3)_3CX$ the values of μ_M are also not identical, nor are μ_π, nor even $\Delta_H + \mu_\pi$, since the assumption that the moments μ_i induced by the substituent X in the benzene ring and the group $C(CH_3)_3$ are the same is arbitrary. To determine the exact value of Δ_H at the present time is difficult, in view of the absence of the necessary experimental values of the moments of the aliphatic and aromatic C−H bonds. We can only say with confidence that $0.4 > \Delta_H < 0.2$. However, the limits for use of the Sutton rule can be determined, knowing only orienting values for Δ_H.

In the molecule of C_6H_5X depending on the character of the substituent X, there are four possible variants of paired conjugated moments μ_σ and μ_π (the direction of moment μ_i always agrees with that for moment μ_σ which determines the resulting moment of the molecule). We have seen that a negative value for the moment shows the negative end of the dipole on the substituent X ($\overset{+}{C}-\overset{-}{X}$), a positive value shows the reverse ($\overset{-}{C}-\overset{+}{X}$).

Values of μ_M and $\mu_\pi + \mu_i$, Calculated from Dipole Moments of C_6H_5X and CH_3X (in D) Determined in Benzene (we give in parenthesis the values obtained on the basis of the Stark effect)

X	Mechanism of electron reaction with ring	$\mu(C_6H_5X)$	$\mu(CH_3X)$	μ_M	$\mu_\pi + \mu_i$	μ_i
CN	$-M-I$	−4,02	−3,47	−0,55	−0,85	< 0
NO_2	$-M-I$	−4,00	−3,15	−0,85	−1,15	< 0
NC	$-M-I$	−3,53	(−3,83)	+0,30	±0,00	> 0(?)
CF_3	$-M^*-I$	−2,60	(−2,32)	−0,28	−0,58	< 0
$SiCl_3$	$-M-I$	−2,41	−1,87	−0,54	−0,84	< 0
$SiBr_3$	$-M-I$	−2,36	−1,86	−0,50	−0,80	< 0
CCl_3	$-M^*-I$	−2,04	−1,57	−0,47	−0,77	< 0
Cl	$+M-I$	−1,58	−1,86	+0,28	−0,02	< −0,02
Br	$+M-I$	−1,56	−1,82	+0,26	−0,04	< −0,04
F	$+M-I$	−1,48	−1,79	+0,31	+0,01	< 0
I	$+M-I$	−1,38	−1,66	+0,28	−0,02	< −0,02
C≡CH	$+M-I$	−0,66	−0,75	+0,09	−0,21	< −0,21
CH_3	$+M^*+I$	+0,37	0,00	+0,37	+0,07	> 0< 0,07
$C(CH_3)_3$	$+I$	+0,42	0,00	+0,42	+0,12	+ 0,12
$Si(CH_3)_3$	$-M+I$	+0,44	0,00	+0,44	+0,14	> +0,14

*Effect of σ, π-conjugation.

$C_6H_5 \overset{+}{\leftarrow} X$ (combination of +M and +I effects). $\mu_M = \Delta_H + \mu_\pi + \mu_i$. In this case the Sutton rule is always obeyed, since $\mu_\mu > 0$ at any value of μ_i and Δ_H.

$$C_6H_5 \longrightarrow X \quad (+M-I)\cdot \mu_M = \Delta_H + \mu_\pi - |\mu_i|.$$

$\mu_M > 0$, if $\mu_\pi > |\mu_i| - \Delta_H$. The rule is obeyed in all known cases (X- halogen, C≡CH, etc.), since the value of $|\mu_i| - \Delta_H$ is close to 0 or is a negative value.

$$C_6H_5 \longrightarrow X \quad (-M-I)\cdot \mu_M = \Delta_H - |\mu_\pi + \mu_i|\cdot \mu_M < 0 \quad \text{if} \quad |\mu_\pi| > \Delta_H - |\mu_i|.$$

*If instead of C_6H_5X we start from p-IC_6H_4X, then $\Delta = \mu(C_{al}-H) - \mu(C_{ar}-I)$.

The rule is not justified in the case of substituents which have a small -M effect, which, perhaps includes the group N≡C (however, see below).

$$C_6H_5 \leftarrow X(-\dot{M} + I)\cdot\mu_M = \Delta_H + \mu_i - |\mu_\pi|\cdot\mu_M < 0 \quad \text{if} \quad |\mu_\pi| > \Delta_H + \mu_i.$$

This is just the case when the Sutton rule does not justify itself ($X = Si(CH_3)_3$, $Ge(CH_3)_3$). It is incorrect also if the substituent has only a +I-effect ($C(CH_3)_3$, $Pb(CH_3)_3$, etc.), since $\Delta_H \neq \mu_i$.

Knowing the value of Δ_H, we can determine from μ_M the sum of the moments $\mu_\pi + \mu_i$, which characterizes the perturbations in the nucleus caused by substituent X. Values for this sum are given in the table (the value of Δ_H is estimated at 0.30D). The last column of this table shows that in all cases except for the group NC, the direction of the vector μ_i agrees with the direction of the inductive moment of the substituent X. In the case where X = NC and some other -M substituents the value $\mu_\pi + \mu_i$ evidently indicates the effect of σ, π-conjugation in the molecule of CH_3X which for simplicity we disregarded in the conclusions from equation (3).

SUMMARY

We have considered a method for determining the direction of the mesomeric effect of substituents from the dipole moments of C_6H_5X and CH_3X (according to Sutton) and have established the limits of its usefulness.

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INVESTIGATION OF THE HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF BUTYLPHENOLS UNDER HYDROGEN PRESSURE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1691-1695, September, 1961
Original article submitted January 9, 1961

The homogeneous destructive hydrogenation of higher phenols permits the preparation of phenol and its lower homologues. In this the rate of the process and the composition of the reaction products are determined by the structure of the alkyl group and its position in the molecule of the starting alkylphenol. We observed dealkylation of butylbenzene during an earlier investigation of the homogeneous destructive hydrogenation of tetralin [1]. The behavior of cresols and propylphenols under the conditions of homogeneous destructive hydrogenation were investigated by Gonikberg and Li Huan-Nyan' [2]. These authors found in particular that ~40 mol.% of phenol could be obtained from ortho n- and iso-propylphenols. In the present work homogeneous destructive hydrogenation of ortho and para n-butylphenols was studied as well as of para sec-butylphenol under hydrogen pressure.

EXPERIMENTAL

Ortho and para n-butylphenols were synthesized by reduction of the corresponding ketones by Clemmensen's method. The ketones were prepared by condensation of butyric acid chloride with phenol and subsequent rearrangement of the ether formed with aluminum chloride into the ortho and para hydroxybutyrophenones [3]. After careful fractional distillation each ketone was separately reduced; the reduction products were redistilled in vacuum through a rectifying column with an efficiency of 30 theoretical plates to give: ortho n-butylphenol, b.p. 124-125° (20 mm); n_D^{20} 1.5215; para n-butylphenol, b.p. 137-138° (20 mm); n_D^{20} 1.5185.

The starting para sec-butylphenol was prepared by isomerization of n-butylphenyl ether with aluminum chloride. The resultant product was redistilled through a column [b.p. 131-132° (20 mm)]; it crystallized in the process as long white needles. After pressing on a porous plate and crystallizing from petroleum ether, it had a m.p. 61-62°. Found: C 79.65, 79.73; H 9.20, 9.43%. $C_{10}H_{14}O$. Calculated: C 80.00; H 9.40%.

Experiments were carried out in a reactor of stainless steel, capacity 120 ml, by the usual procedure [1]. For each experiment 40 g of the starting butylphenol was placed in the reactor. In experiments with n-butylphenols the initial pressure of hydrogen was 200 and 400 atm (operating pressure ~400 and 700 atm respectively); experiments were carried out at a temperature of 400°; duration of experiments 3 hours. The ethereal solution of the combined reaction products from three parallel experiments was dried with anhydrous sodium sulfate, after which fractional distillation was carried out through a rectifying column of the above mentioned efficiency. Benzene, toluene, ethylbenzene, and propylbenzene were distilled at atmospheric pressure (up to 175°); then the distillation was carried out under vacuum (20 mm); during which first of all a phenol fraction (~85° (20 mm)] distilled over, which crystallized in the process; obviously the n-butylbenzene content in this fraction was very small. In Fig.1 is given the curve for the vacuum distillation of the reaction products from ortho n-butylphenol at 440° and initial hydrogen pressure 400 atm. On this curve flat sections are clearly seen at temperatures of ~85° (phenol), 90° (ortho cresol), 98-102° (ortho ethylphenol) and also ~125° (starting ortho n-butylphenol). The content of ortho n-propylphenol in the reaction products was apparently small, since on the curve a flat section was not observed at 120° (20 mm). Ortho cresol was

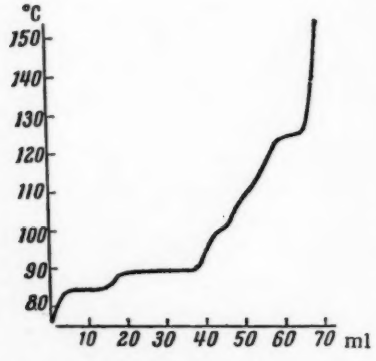

Fig. 1. Distillation curve of the reaction products from ortho n-butylphenol.

identified in the fraction with b.p. 89.5-95° (20 mm) as its derivative with monochloracetic acid m.p. 150-151°. A test portion mixed with ortho cresoxyacetic acid did not depress the melting point. Ortho n-ethylphenol in the fraction with b.p. 95-105°(20 mm) was also identified as the ortho ethyl phenoxyacetic acid m.p. 140-141° (corresponding with the literature value [4]).

In Fig. 2 is shown the curve for the vacuum distillation of the reaction products from para n-butylphenol at 440° and initial hydrogen pressure 400 atm. On this curve are seen plateaux, corresponding to phenol, para cresol (100-102°), para ethylphenol (114-115°) and starting material (137-138°). Para cresol was identified in the fraction with b.p. 95-105° (29 mm) as para cresoxyacetic acid m.p. 135-136°; the melting point of a test mixture was not depressed. Paraethylphenol crystallized out from the fraction b.p. 110-120°(20 mm); after pressing out on a porous plate it had m.p. 45-46°, which corresponds to the literature value [5]. The derived para ethylphenoxyacetic acid had m.p. 96°. Found: C 66.51, 66.66; H 6.66, 6.73%. $C_{10}H_{12}O_3$. Calculated: C 66.62; H 6.77%.

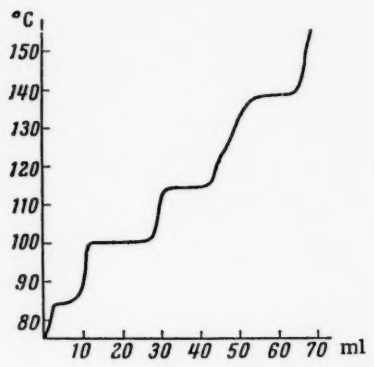

Fig. 2. Distillation curve of the reaction products from para n-butylphenol.

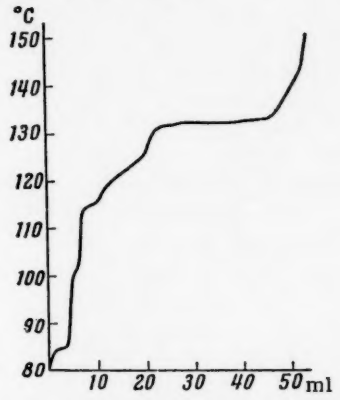

Fig. 3. Distillation curve of the reaction products from para sec-butyphenol.

Experiments with para sec-butylphenol were carried out at 440° and initial hydrogen pressures of 200, 400, and 600 atm (operating pressures ~400, 700, and 1100 atm, respectively); duration of experiments, 3 hours. In Fig.3 is shown the distillation curve of vacuum (20 mm) fractionation of the reaction products for an initial pressure of 400 atm, after distilling off alkylbenzenes at atmospheric pressure up to 175°. On the curve together with the plateaus corresponding to phenol (~85°), para ethylphenol (~115°) and the starting para sec-butylphenol (~132°) can be seen a small "step" at 102° (para cresol) and an ascending section at 120-127°. During distillation of the product with b.p. 120-125° (20 mm) it crystallized in the process: after pressing on a porous plate and crystallization from petroleum ether it had m.p. 61-62°, which corresponds with the literature value for para isopropylphenol. Found: C 79.37, 79.30; H 8.83, 8.71%. $C_9H_{12}O$. Calculated: C 79.42; H 8.88%. The derived compound with monochloracetic acid had m.p. 82-83° (from petroleum ether) and was para isopropylphenoxyacetic acid. Found: C 68.23, 68.11; H 7.28, 7.17%. $C_{11}H_{14}O_3$. Calculated: C 68.04; H 7.27%. From the fraction with b.p. 125-130° (20 mm) with mono chloracetic acid a compound was obtained with m.p. 68-69° which was para n-propylphenoxyacetic acid. Found: C 68.27, 68.24; H 7.30, 7.13%. $C_{11}H_{14}O_3$. Calculated: C 68.04; H 7.27%. We also obtained an identical compound from the fraction with b.p. 125-131° (20 mm), separated from the reaction products of para n-butylphenol.

During homogeneous destructive hydrogenation of the isomeric butylphenols the formation of higher boiling reaction products (see table) was observed, which were apparently mainly polyalkylphenols. For example, by vacuum fractionation of the residues after distilling off the starting ortho n-butylphenol the following fractions were obtained: b.p. 125-145° (9 mm), mol. wt. 176; b.p. 145-185° (9 mm), mol. wt. 197; b.p. 160-185° (1 mm), mol. wt. 210. Data on the composition of the liquid reaction products based on the distillation curves and identification of the compounds in the individual fractions are given in the table.

As seen from the data of the table, according to the rate of total conversion under the conditions of homogeneous destructive hydrogenation the investigated alkylphenols follow the series: ortho n-butylphenol > para n-butylphenol > para sec-butylphenol. It may be noted that his sequence is analogous to that observed for the isomeric propylphenols: ortho n-propylphenol > para n-propylphenol > para isopropylphenol [2]. The results given in the table lead to the conclusion than an increase in the hydrogen pressure results in some increase in the rate of conversion of

the butylphenols and also in an increase in the contents of phenol and alkylbenzene in the reaction products and decrease in yield of high boiling residue.

Homogeneous Destructive Hydrogenation of Butylphenols at 440°, 3 hours

Starting phenol	o-n-butyl-phenol		p-n-butyl-phenol		p-sec-butyl-phenol		
Initial pressure atm	200	400	200	400	200	400	600
Yield of liquid products wt.% on initial phenol	78.0	76.2	80.0	77.4	84.4	85.4	77.8
Including:							
Benzene and its homologues	6	13	5	11	6	9	17
Phenol	9	15	5	10	5	8	12
o-Cresol	28	20	–	–	–	–	–
p-Cresol	–	–	20	16	2	3	3
o-Ethylphenol	8	7	–	–	–	–	–
p-Ethylphenol	–	–	18	13	10	9	7
o-n-Propylphenol	9*	7*	–	–	–	–	–
p-n-Propylphenol	–	–	3	5	5**	9**	12**
p-Isopropylphenol	–	–	–	–	5**	9**	12**
o-n-Butylphenol	8	8	–	–	–	–	–
p-n-Butylphenol	–	–	16	13	–	–	–
p-sec-Butylphenol	–	–	–	–	34	31	14
Residue	7	6	12	8	18	11	6

*Yield of fraction distilled over containing o-n-propylphenol mixed with starting o-n-butylphenol.

**Principally p-isopropylphenol.

DISCUSSION OF EXPERIMENTAL RESULTS

A radical-chain mechanism was considered for the homogeneous destructive hydrogenation of aromatic hydrocarbons and alkylphenols in a number of earlier publications (see, for example, [1,2,6]). According to the ideas we have developed, the rate of generation of reaction chains is determined by the energy of cleavage of the weakest bond in the molecule of the starting compound; development of the chains is visualized as an interaction of atomic hydrogen with the molecules of this compound and subsequent reaction of the radicals formed with molecular hydrogen. As a result of the generation of chains alkylphenols are formed with shorter side chains compared with the original alkylphenol; formation of phenol occurs predominantly as a result of the reaction in the development of the chains. Thus, by knowing the composition of the products from homogeneous destructive hydrogenation of an alkylphenol at different hydrogen pressures it is possible to gain knowledge of the weakest bonds in the molecule.

On the basis of the results in the table it may be concluded that in ortho and in para n-butylphenols the weakest bonds are $HOC_6H_4CH_2-CH_2CH_2CH_3$ and $HOC_6H_4CH_2CH_2-CH_2CH_3$. In para sec-butylphenol judging by the results we obtained the weakest bonds are $HOC_6H_4CH(CH_3)-CH_2CH_3$ and $HOC_6H_4CH(CH_3)CH_2CH_3$, the cleavage of which leads to the formation of para ethylphenol and para isopropylphenol. The bond of $HOC_6H_4CH(C_2H_5)CH_3$ was found to be stronger, during cleavage of which n-propylphenol (in small quantities) was observed. In contrast to the products of homogeneous destructive hydrogenation of butylphenol formation of paracresol was hardly observed, which is in complete accordance with the proposed scheme.

Under the conditions studied the yield of alkylphenols with shorter side chains compared with the starting material was considerably greater than the yield of phenol. This indicates that at the temperatures used and hydrogen pressures prevailing there is no dealkylation process but a thermal decomposition of the alkylphenol at the weakest bond with subsequent saturation of the free valencies with hydrogen. The higher the pressure, the greater the part played by the dealkylation process which is clearly illustrated by the data in the table. If the results obtained are compared with the data from the investigation of the homogeneous destructive hydrogenation of the isomeric cresols and propylphenols [2], then it must be concluded that according to the increase in the number of carbon atoms in

the side chain of the alkylphenol thermal decomposition processes begin to prevail all the more over reactions leading to cleavage of the alkyl radical from the aromatic nucleus.

SUMMARY

1. Homogeneous destructive hydrogenation of three isomeric butylphenols at 440° and high hydrogen pressures was investigated. The reaction rate decreased in the series o-n-butylphenol > p-n-butylphenol > p-sec-butylphenol. The difference in the rate of total conversion was determined predominantly by the stage in which there was thermal cleavage of the weakest bond of the alkyl group.

2. A rise in hydrogen pressure accelerated the process of homogeneous destructive hydrogenation of butylphenols.

3. The weakest bonds in n-butylphenols were apparently the β and γ C—C bonds in the alkyl chain; the same was true also for para sec-butylphenol.

4. Comparison of the results obtained led to the conclusion that depending on the increase in the number of carbon atoms in the side chain of the alkylphenol, thermal decomposition processes start to prevail to a greater extent over reactions leading to cleavage of the entire alkyl radical from the aromatic nucleus.

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THE CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS AND THEIR HYDROPOLYMERIZATION UNDER THE INFLUENCE OF CARBON MONOXIDE AND HYDROGEN

COMMUNICATION 32. CONVERSION OF OCTENE-1

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1696-1702, September, 1961
Original article submitted January 28, 1961

In considering the mechanism of catalytic hydropolymerization of olefins under the influence of small amounts of carbon monoxide in the presence of hydrogen, the possiblilty of the formation of alkyl radicals on the catalyst surface was mentioned. Side by side with the transformations leading to growth of the hydrocarbon chain, these radicals can undergo decomposition with formation of an adsorbed molecule of a lower olefin and a smaller alkyl radical on the surface [1]. Such a decomposition, characteristic of low stability radicals of high molecular weight, is apparently the cause of the formation of hydrocarbons having a smaller number of carbon atoms than the original olefin ("low boiling components") and is the greater, the higher the molecular weight of the latter. Thus, in the case of n-butanes 2-4% of the original olefin is converted to C_1 - C_3 hydrocarbons [2,3] and in the case of hexene-1, 8% to C_5 and 1% to C_1 - C_4 hydrocarbons [4]. Together with these there are also produced "high boiling components," i.e., hydrocarbons with a greater number of carbon atoms than in the original olefin. In experiments with hexene-1 such hydrocarbons are produced up to 23% of the original olefin [4].

An unusual feature of these "high boiling" hydrocarbons is that they give rise not only to true polymers and their hydrogenation products, but also to hydrocarbons with a non-multiple number of carbon atoms in the molecule compared with the original olefin. Obviously, the alkyl radicals formed during the decomposition process, mentioned above, enter into the reaction leading to a lengthening of the carbon chains. The formation of a large number of higher hydrocarbons with a non-multiple number of carbon atoms compared to the original olefin, is most clearly observed during the hydropolymerization of isooctene,* the highest molecular weight olefin which has been subjected to this reaction so far. This is quite clear since it is possible for a larger number of higher hydrocarbons with a non-multiple number of carbon atoms to arise in the case of higher olefins than for lower olefins. In fact the number of equal hydrocarbons possible in a series between, for example, two adjacent true polymers for any olefin C_nH_{2n} is equal to n -1, i.e., it increases with increase of the number of carbon atoms in the molecule; for ethylene it is equal to 1, for hexene 5, for octene 7.

In this connection it was of interest to investigate the conversion of octene -1 in the hydropolymerization reaction under the influence of CO. As is usually done in the investigation of other olefins, in the present work the conversions occurring under these conditions were studied of octene -1 alone, its mixture with hydrogen, and finally its mixture with hydrogen and carbon monoxide. In addition to this the joint hydropolymerization of octene -1 with ethylene was studied.

EXPERIMENTAL

The apparatus, order of carrying out experiments, composition and preparation of catalyst were as in previous papers [1-4]. Octene -1 was synthesized by thermal decomposition of ocylacetate by van Pelt and Wibaut's method [5] and had b.p. 120.7-121.0° (760 mm); n_D^{20} 1.4088; d_4^{20} 0.7149, and Kaufman's bromine number was 141.7%(99.4% unsaturated). The literature gives for octene [6]: b.p. 121.28° (760 mm); n_D^{20} 1.4087; d_4^{20} 0.7149. Octene -1 was fed from an automatic buret into the contact tube of 10 mm internal diameter, containing a charge (5 g CO volume 22

*Observations by Ya. T. Eidus and H. I. Ershova in 1948.

ml, length of layer 31 cm) of a percipitated Co-clay hydropolymerization catalyst [7]. Reduction and regeneration of the catalyst was carried out in a stream of electrolytic hydrogen at 450° for 5 hours. All experiments, duration 5-10 hours, were carried out at 190° and at atmospheric pressure in a flow-through system. The reaction products were collected in two receivers at room temperature and at -80°, respectively. The emerging gas was collected in a gasometer. The liquid catalyzate after drying and boiling with metallic sodium (for 1 hour) was fractionated through a column with an efficiency of 30 theoretical plates up to 150°C, and the residue from a small Wurtz flask. The conditions of carrying out the experiments and some of the results are given in Table 1, the results of the fractional distillation of the catalyzates in Figs 1-2 and in Tables 2-8. In Table 9 are collected the results obtained in this work.

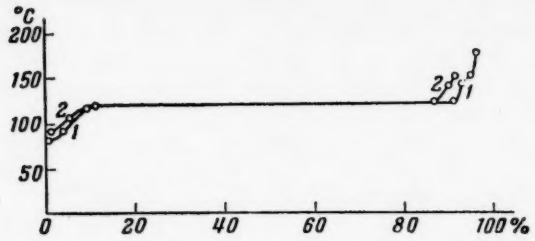

Fig. 1. Distillation curves of the catalyzates: 1) experiment 2; 2) experiment 5.

Octene -1. Experiment 1 was carried out with octene -1 alone, in the absence of H_2 and CO, on freshly reduced contact 1. Before the experiment in order to displace hydrogen from the system 9l N_2 was passed at 190°. The catalyzate obtained in experiment 1 (b.p. 120-121°; d_4^{20} 0.7152; n_D^{20} 1.4099, bromine number 141.9) was practically unchanged octene -1.

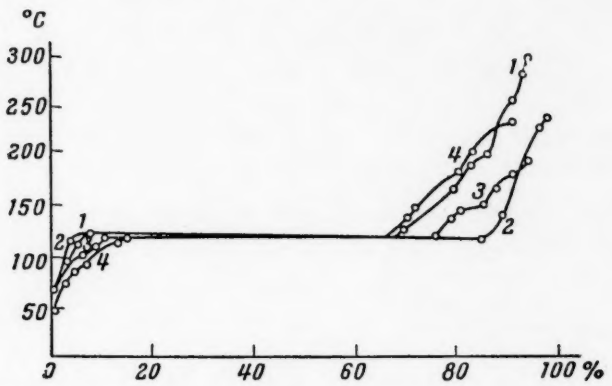

Fig. 2. Distillation curves of the catalyzates: 1) experiment 3; 2) experiment 4; 3) experiment 6; 4) experiment 7.

Octene -1—hydrogen. Two experiments were carried out with a C_8H_{16} - H_2 binary mixture; experiment 2 on regenerated contact 1 and experiment 5 on freshly reduced contact 4 (Table 1). In the feed vapor-gas mixture the ratio $(H_2/C_8H_{16})_{feed}$ was 1.1 and 3.2, respectively. The catalyzates were fractionated to give 55 (Table 2) and 27 ml (Table 3).

In experiment 2, 65% of the octene -1 was hydrogenated to octane, ~80% in experiment 5. The literature gives for octane [6]: b.p. 125.67°; n_D^{20} 1.3974; d_4^{20} 0.7025. Fraction I containing low boiling hydrocarbons (C_7), comprised 4.4-5.5%, and fraction III corresponding to high boiling components, 7.3-7.7% of the catalyzate. The gaseous hydrocarbons (C_1—C_4) formed comprised 1.7-3.2 mol. % of the initial octene -1. In Fig.1 are shown distillation curves of the catalyzates from experiments 2 (curve 1) and 5 (curve 2).

Octene -1—Hydrogen—Carbon monoxide. Experiments 3, 4, and 6 (Table 1) were carried out with a ternary mixture. Experiment 3 was carried out on freshly reduced contact 2 with the ratio $(H_2/C_8H_{16})_{feed}$ 1.05, $(H_2/CO)_{feed}$ 7.8 and a 6.2% CO content in the feed vapor-gas mixture (Table 1). The distilled catalyzate, amounting to 90 ml (Table 4, Fig.2, curve 1) contained 70% octane and octene in a 1:2 ratio, 3.1% low boiling hydrocarbons (C_5—C_7, fraction I) and 24.5% high boiling hydrocarbons (C_9 and above, fractions VI-VIII). In addition 7.5 ml of solid paraffin with b.p. 295-345° was removed from the surface of the catalyst by ether extraction. Taking into account the solid paraffin the content of high boiling components was 31.1%. In the formation of the higher hydrocarbons 9 mole-

cules of octene -1 take part per molecule of CO, (yield per initiator equals 9). 0.8 Mo. % of the introduced octene -1 comes over in the gaseous hydrocarbons. In order to ascertain the distribution of hign boiling hydrocarbons with respect to molecular weight, a portion of these hydrocarbons with b.p. above 125° was completely hydrogenated on a platinum catalyst and the 31 ml of hydrogenizate (n_D^{20} 1.4202; d_4^{20} 0.7455; bromine number 0.0) was distilled from a small Wurtz flask to give fractions of approximately the same molecular weight. For each fraction n_D^{20}, d_4^{20}, and the average molecular weight by the cryoscopic method in benzene solution were determined. The results obtained, given in Table 5, indicate the presence of hydrocarbons intermediate between the original hydrocarbon and its dimer and higher boiling hydrocarbons. Experiment 4 was carried out on freshly reduced contact 3 with $(H_2/C_8H_{16})_{feed}$ 0.8; $(H_2/CO)_{feed}$ 1.9 and a content of 18.6% CO in the feed vapor-gas mixture (Table 1). In the distillation 48 ml of catalyzate were collected (Table 6, Fig.2, curve 2). The octane and octene (ratio 1:2) content of the mixture was 85.5% (fraction II), low boiling hydrocarbons (C_7) 2.1%, high boiling components 12.1%. The yield per initiator was 1. 0.9 mol % of the original octene -1 was converted into gaseous C_1-C_4 hydrocarbons.

TABLE 1. Experiments with Octene -1

Number of		Introduced octene -1 ml	Feed vapor-gas mixture				Collected liquid catalyzate vol % on introduced octene	Reacted 1		Gases formed l	
			volume Rate hours^{-1}	Composition vol%							
Contract	Expt.			C_8H_{16}	H_2	CO		H_2	CO	C_nH_{2n}	C_nH_{2n+2}
1	1	50	70	100	—	—	96,0	—	—	—	—
1*	2	60	111	45,1	54,9	—	96,3	8,8	—	0,3	0,4
2	3	113	142	45,7	48,1	6,2	96,4	7,5	0,7	0,1	0,8
3	4	60	146	45,2	36,2	18,6	94,3	4,0	1,1	0,4	0,2
4	5	30	93	23,8	76,2	—	91,0	6,3	—	0,2	0,5
4*	6	35	74	26,5	63,7	9,8	89,7	7,7	1,4	0,1	0,8
5	7	30	95	21,6	44,3	7,8**	103,7	6,1	0,55	—	2,2

* Before the experiment the contact was regenerated at 450° for 5 hours.

** In the mixture there was still 26.3% C_2H_4 present.

TABLE 2. Fractions of the Catalyzate from Experiment 2

Number of fraction	Boiling range °C at 760 mm of Hg	Content vol %	n_D^{20}	d_4^{20}	Bromine number	Content of unsatd. hydrocarbons	C_n
I	82—103	5,5	1,3875	0,6767	41,2	25,7	C_7
II	103—125	85,5	1,4012	0,7060	35,7	26,5	C_8
III	125—183	7,3	1,4129	0,7296	16,9		C_9
Residue and loss		1,7					and above
Original catalyzate		100	1,4011	0,7067	33,4		

TABLE 3. Catalyzate Fractions from Experiment 5

Number of fraction	Boiling range °C at 760 mm of Hg	Content vol %	n_D^{20}	d_4^{20}	Bromine number	Content of unsatd. hydrocarbons	C_n
I	92—101	4,4	—	—	—		C_7
II	101—125	80,8	1,3968	0,7005	4,5	2,8	C_8
III	125—147	7,7	1,4097	0,7275	3,2		C_9
Residue and loss		7,1					and above
Original catalyzate			1,3976	0,7022	3,6		

Experiment 6 was carried out on regenerated contact 4 with $(H_2/C_8H_{16})_{feed}$ 2.4, $(H_2/CO)_{feed}$ 6.5 and a content of 9.8% CO in the feed vapor-gas mixture. On distillation through the column 30 ml of catalyzate were obtained (Table 7, Fig.2, curve 3) in which was present ~70% of octanes and octenes, 4.3% of low boiling (C_7) and 19.3%

of high boiling hydrocarbons. Yields per initiator was equal to 1.2. Yield of gaseous hydrocarbons (C_1–C_4) was 2.6 mol.% on the original octene -1.

Octene-1 – Ethylene – Hydrogen – Carbon Monoxide. Experiment 7 was carried out with the mixture $C_8H_{16}:C_2H_4:H_2:CO = 2.8:3.3:3.5:7.1$ on freshly reduced contact 5 (Table 1) 74.3% of the octene-1 reacted, 40% of it was hydrogenated to octane. 93.8% of the ethylene reacted: 32.5% was converted to ethane and 61.3% was hydropolymerized. The catalyzate, the yield of which amounted to 103.7% on the volume of the original octene -1, yielded 28 ml when distilled through the column (Table 8, Fig.2, curve 4). It contained 55% of octane and octene (in 1:1 ratio), 7.2% of hydrocarbons boiling below octene -1 (fraction I) and 25.7% boiling above octane (fraction III). The yield per initiator was 2.5 with respect to octene and 5 with respect to ethylene.

TABLE 4. Catalyzate Fractions from Experiment 3

Number of fraction	Boiling range °C at 760 mm of hg	Content vol. %	n_D^{20}	d_4^{20}	Bromine number	Content of unsatd. hydrocarbons	C_n
I	50—100	3,1	1,3861	0,6658	136,9	72	C_5—C_7
II	100—120	9,3	1,4039	0,7054	113,5	79	C_8
III	121—122	14,4	1,4068	0,7116	110,0	77	C_8
IV	122,5—123,6	32,2	1,4061	0,7116	86,7	60	C_8
V	123,6—124,7	14,4	1,4060	0,7107	80,8	56	C_8
VI	124,7—151,0	5,8	1,4100	0,7198	74,1	—	C_9
VII	151,0—200	7,6	1,4179	0,7361	57,4	—	C_{10}—C_{11}
VIII	200—295	11,1	1,4368	0,7758	24,6	—	C_{11}—C_{17}
Residue and loss		2,1					
Original catalyzate		100	1,4107	0,7197	85,1		

TABLE 5

Number of fraction	Boiling range °C at 760 mm hg	Content of high boiling components in the fraction Vol. %	n_D^{20}	d_4^{20}	Mol. wt. found	Mol. wt. calculated	C_n
I	130—152	8,4	1,4032	0,7146	127	128,25	C_9
II	152—176	21,6	1,4070	0,7208	146	142,28	C_{10}
III	176—198	14,5	1,4130	0,7326	151,5	156,30	C_{11}
IV	198—220	11,6	1,4198	0,7469	168,5	170,33	C_{12}
V	220—238	2,6	1,4249	0,7559	183,5	184,35	C_{13}
VI	238—256	4,5	1,4278	0,7627	200,5	198,38	C_{14}
VII	256—272	5,2	1,4301	0,7681	216	212,41	C_{15}
VIII	272—290	5,8	1,4342	0,7782	226	226,43	C_{16}
IX	290—304	7,7	1,4385	0,7883	250	240,46	C_{17}
X	>304	5,2	—	—	329,5	324,38	C_{23}
XI	solid paraffin	12,9	—	—	675	675,26	C_{48}

From the results presented it is seen (Table 9) that octene -1 in the absence of H_2 and CO is practically unchanged under the reaction conditions for hydropolymerization In mixtures with hydrogen, hydrogenation of octene -1 to octane principally occurs, whereby the C_8H_{18}/C_8H_{16} ratio in the catalyzate grows larger with increase in the $(H_2/C_8H_{16})_{feed}$ ratio; generally the content of octane and octene was 81-85%. In the catalyzates there were also small amounts (4.4-5.5%) of low boiling hydrocarbons starting to boil at 80-90° and (7.3-7.7%) of high boiling hydrocarbons with a final boiling point 147-183°. Addition of CO to the binary mixture of C_8H_{16}–H_2 led to a sharp increase in the yield of the high boiling and some reduction in the yield of the low boiling hydrocarbons. The ratios $(H_2/CO)_{feed}$ and $(H_2/C_8H_{16})_{feed}$ play an essential part. The optimum conditions for formation of higher hydrocarbons under the influence of CO were observed with $(H_2/C_8H_{16})_{feed} = 1$ and $(H_2/CO)_{feed} = \sim 8$ (experiment 3). Under these conditions there was found in the catalyzate (including solid paraffins 3% of low boiling hydrocarbons, starting to boil at 50° and 31% of high boiling hydrocarbons with a final boiling point of 345°; intermediate C_9–C_{16} hydrocarbons as well as those of higher molecular weight being present. For each molecule of CO entering into reaction to

form higher hydrocarbons, 9 molecules of octene -1 also took part. With $(H_2/C_8H_{16})_{feed}$ 2.4 and $(H_2/CO)_{feed}$ 6.5 (experiment 6), 4.3% of low boiling hydrocarbons with initial boiling point 67° and 19.3% of high boiling hydrocarbons with final boiling point 220° were found in the catalyzate. The yield of octane was greatly increased, and was present in the catalyzate with octene in the ratio 6.7:1.

TABLE 6. Catalyzate Fractions from Experiment 4

Number of fraction	Boiling range °C at 760 mm of hg	Content vol. %	n_D^{20}	d_4^{20}	Bromine number	Content of unsatd. hydrocarbons	C_n
I	60—100	2,1	1,3941	0,6853	132,2	81	C_7
II	100—125	85,4	1,4079	0,7118	95,2	61	C_8
III	125—243	12,1	1,4240	0,7492	49,1		C_9 and above
Residue and loss		0,4					
Original catalyzate		100	1,4099	0,7169	88,4		

TABLE 7. Catalyzate Fractions from Experiment 6

Number of fraction	Boiling range °C at 760 mm of hg	Content vol. %	n_D^{20}	d_4^{20}	Bromine number	Content of unsatd. hydrocarbons	C_n
I	67—100	4,3	—	—	—	—	C_7
II	100—125	71,7	1,3974	0,7014	19,0	13	C_8
III	125—220	19,3	1,4180	0,7418	5,2		C_9 and above
Residue and loss		4,7					
Original catalyzate		100	1,4026	0,7099			

TABLE 8. Catalyzate Fractions from Experiment 7

Number of fraction	Boiling range °C at 760 mm of hg	Content vol. %	n_D^{20}	d_4^{20}	Bromine number	Content of unsatd. hydrocarbons	C_n
I	46—100	7,1	1,3836	0,6660	93,5	50	C_6—C_7
II	100—125	55,4	1,4033	0,7073	65,2	46	C_8
III	125—245	25,7	1,4228	0,7504	24,4		C_9 and above
Residue and loss		11,7					
Original catalyzate		100	1,4089	0,7160	56,5		

By maintaining $(H_2/C_8H_{16})_{feed}$ close to unity (0.8) and by greatly reducing $(H_2/CO)_{feed}$ to 1.9 (experiment 4) the content of high boiling hydrocarbons in the catalyzate was sharply decreased to 12.1% (final boiling point 243°) and the low boiling hydrocarbons to 2.1% (initial boiling point 60°). In experiments 4 and 6 for one molecule of CO taking part in the formation of higher hydrocarbons only 1 molecule of octene -1 was involved. With octene -1 and ethylene both present in the feed vapor-gas mixture in approximately equivalent proportions with $(H_2/C_nCH_{2n})_{feed}$ 0.9 and $(H_2/CO)_{feed}$ 5.7 hydrocopolymerization of both olefins occurred. This follows from the fact that in the catalyzates, obtained in the absence of ethylene, the total content of octane and octene amounted to not less than 70%, whereas in experiment 7 altogether it equalled 55%. The content of high boiling hydrocarbons with final boiling point 245° was 25.7% and of low boiling components with initial boiling point 46° was 7.2%

SUMMARY

1. The catalytic conversion of octene-1 in the presence of hydrogen and of a mixture of hydrogen and carbon monoxide was investigated.

TABLE 9

Number of experiments	In feed vapor-gas mixture: CO content %	In feed vapor-gas mixture: (H_2, C_nH_{2n}) feed	In feed vapor-gas mixture: (H_2/CO) feed	In catalyzate: C_8H_{16} + C_8H_{18} content vol. %	In catalyzate: volume ratio C_8H_{16} / C_8H_{18}	In catalyzate: high boiling components: vol. %	In catalyzate: high boiling components: final boiling point °C	In catalyzate: low boiling components: vol. %	In catalyzate: low boiling components: initial boiling point °C	Gaseous C_1 - C_4 hydrocarbons mol. % formed from original C_8H_{16}
1	0,0	0,0	—	~100	0,0	—	—	—	—	0,0
2	0,0	1,1	—	85,5	3	7,3	183	5,5	82	1,7
5	0,0	3,2	—	80,8	21	7,7	147	4,4	92	3,2
3	6,2	1,05	7,7	70	0,5	31,1	345	3,1	50	0,8
4	18,6	0,8	1,9	85,5	0,5	12,1	243	2,1	60	0,9
6	9,8	2,4	6,5	70	6,7	19,3	220	4,3	67	2,6
7	7,8	0,4	5,7	55	1	25,7	245	7,2	46	—

2. Under optimum conditions up to 30% of octene-1 underwent reaction with formation of intermediate hydrocarbons from C_9 to C_{16} as well as of higher boiling components.

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THE STRUCTURE OF N-BENZYLPYRIDINIUM-γ-CYCLOPENTADIENYLIDE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1703-1704, September, 1961
Original article submitted November 30, 1960

Some years ago in the reaction of lithium cyclopentadiene with benzylpyridinium chloride we obtained N-benzylpyridinium-γ-cyclopentadienylide (I), whose structure we did not give in our paper [1]. In the present report this information is given.

The empirical formula of the substance $C_{15}H_{17}N$ was established on the basis of elementary analysis and molecular weight [1].

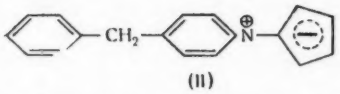
The presence in (I) of pyridine and cyclopentane rings was shown by the reaction of catalytic hydrogenation under conditions which excluded the hydrogenation of the benzene ring. The substance absorbed five moles of hydrogen with formation of a tertiary amine, isolated as the chloroplatinate $C_{17}H_{25}N \cdot {}^1/_2H_2PtCl_{16}$ and the methiodide $C_{18}H_{28}NI$ [1,2].

The γ-position of the substituent in the pyridine ring of (I) was determined by its oxidation to γ-pyridinecarboxylic (isonicotinic) acid [3].

(I)

The oxidation was carried out with potassium permanganate in dilute sulfuric acid. The thus formed γ-pyridine carboxylic acid was isolated and purified by the method used by Chichibabin in the oxidation of benzylpyridine [4] and after sublimation had m.p. 320° (in a sealed capillary). A mixed sample with known γ-pyridine carboxylic acid gave no melting point depression.

The evidence that the cyclopentadiene ion occurred in the γ-position, and not the benzyl group, was obtained by comparison of the properties of substance (I) and its isomer, γ-benzylpyridinium-N-cyclopentadienylide (II) [5]



(II)

Compounds (I) and (II) differed sharply from each other in properties (color, decomposition temperature, ultraviolet absorption spectra [5,6]).

SUMMARY

We have shown the structure of N-benzylpyridinium-γ-cyclopentadienylide which is formed in the reaction of lithium cyclopentadiene and benzylpyridinium chloride.

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HIGH TEMPERATURE HYDROGENATION DESTRUCTION OF XYLENES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1704-1705, September, 1961
Original article submitted February 24, 1961

The chemistry of hydrogenation of xylenes at high temperature, 460°, and hydrogen pressures of 25 and 50 atm has been studied in detail in the presence of nickel-alumina catalysts [1]. There are results in the literature for hydrogenation of m-xylene in the presence of platinum [2] and molybdenum [3] catalysts, and also for a technical mixture of xylenes under pressures up to 10 atm and at temperatures of 400-700° in the presence of different catalysts [4-7] and in a homogeneous process [8]. The main direction of the conversion of the isomeric xylenes is their demethylation and formation of benzene and toluene in amounts which depend on the conditions of the process, temperature, pressure, and catalysts. However, the dependence of the depth of the conversion of xylenes on the position of the methyl substituents in these studies was not investigated sufficiently.

We studied the chemistry of the high temperature hydrogenation of the isomeric xylenes under a pressure of 100 atm at a temperature of 520°, volume rate 1.5 kg/liter · hour, mole ratio of raw material : hydrogen = 1 : 4.0-4.5, in the presence of a catalyst of $MoO_3 + Al_2O_3$ under conditions of a flowing apparatus. The starting hydrocarbons had the following constants: m-xylene, d_4^{20} 0.8629, n_D^{20} 1.4970; p-xylene, d_4^{20} 0.8619; n_D^{20} 1.4960; o-xylene, d_4^{20} 0.8804, n_D^{20} 1.5051, which correspond to the literature values for these compounds. According to the results of spectral analysis, The gases were analyzed by an XT-2 chromatograph. The results which were obtained are given in figure and in the table, in which for comparison we give the results of hydrogenation of toluene under the same conditions.

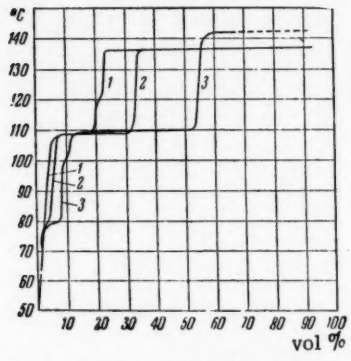

Figure. Curves of rectification of the hydrogenate from m-xylene (1) p-xylene (2) and o-xylene (3) obtained at 100 atm, 520°, volume rate 1.5 kg/liter · hour in the presence of a $MoO_3 + Al_2O_3$ catalyst.

The chief direction of conversion of the isomeric xylenes is the splitting of methyl groups and the formation mainly of toluene. The depth of conversion of the xylenes depends on the position of the methyl groups in the benzene ring and if for m-xylene, 23.7%; for p-xylene, 36.6%; and for o-xylene, 57.2%. In the conversion products there is 50-66% toluene, and hydrocarbons with boiling points higher than the starting one are absent. In the gas, besides hydrogen we found only methane. Coke formation was 0.007% of the hydrocarbon passed. In the hydrogenation of xylenes there was formed a small amount of benzene, 1.2-4.7%, depending on the depth of conversion of the starting hydrocarbon, which is explained by the stepwise mechanism of demethylation. However, comparing the relative content of benzene and toluene in the hydrogenates of toluene and xylenes, taking account of the products of their hydrogenation, we find that in the hydrogenate from the xylenes the relative content of benzenes is higher than in the hydrogenate from toluene, being, for the m-xylene hydrogenate 1 : 4.4; for p-xylene 1 : 5.7; and for o-xylene 1 : 5.5. and for toluene, 1 : 10.3. that is, we can assume that part of the benzene is formed directly from xylene, minimizing the stage of toluene, as a result of splitting two methyl radicals.

In the hydrogenation of xylene the yield of saturated hydrocarbons is 5.4-7.4%, corresponding in chemical composition to the starting aromatic hydrocarbons and products of their demethylation. The yield of dimethylcyclohexane is decreased from 3.2 to 0.3% with increasing depth of demethylation of the starting xylenes, and methylcyclohexane, on the other hand, increases somewhat, since the content of toluene is increased in the reaction mixture.

The products of isomerization of methyl and dimethylcyclohexanes, di- and trimethylcyclopentanes, have not been observed. Cyclohexane is partly isomerized to methylcyclopentane. Paraffin hydrocarbons do not occur in the hydrogenate.

Results of Hydrogenation of Xylenes and Toluene. Conditions: pressure 100 atm, temperature 520°, volume rate 1.5 kg/liter of catalyst per hour; mole ratio hydrogen to hydrocarbon 4-4.5:1; catalyst $MoO_3 + Al_2O_3$.

Starting hydrocarbon	m-Xylene		p-Xylene		o-Xylene		Toluene	
	Yield, weight % of hydrocarbon							
Composition of hydrogenate	starting	converted	starting	converted	starting	converted	starting	converted
Methane	3.7	15.6	6.3	17.2	10.0	17.5	2.1	13.8
Methylcyclopentane	1:0	4.2	1.0	2.7	1.3	2.3	1.2	7.9
Cyclohexane	1.0	4.2	1.3	3.6	1.1	1.9	1.2	7.9
Methylcyclohexane	2.2	9.3	2.1	5.7	2.8	4.9	5.2	34.2
Dimethylcyclohexane	3.2	13.5	1.0	2.7	0.3	0.5	–	–
Benzene	1.2	5.2	2.1	5.7	4.7	8.2	6.3	41.5
Toluene	12.3	51.9	23.9	65.4	39.0	68.2	84.8	–
m-Xylene	76.3	–	–	–	–	–	–	–
p-Xylene	–	–	63.4	–	–	–	–	–
o-Xylene	–	–	–	–	42.8	–	–	–
Total	100.9	103.9	101.1	103.0	102.0	103.5	100.8	105.3
Yield of hydrogen, %	0.9	3.9	1.1	3.0	2.0	3.5	0.8	5.3

SUMMARY

1. The chief reaction in conversion of xylenes under a pressure of 100 atm at a temperature of 520° in the presence of a $MoO_3 + Al_2O_3$ catalyst is demethylation and formation of toluene.

2. Simultaneously with demethylation occurs a reaction of hydrogenation of the xylenes and the products of their demethylation and isomerization of the six membered naphthenes into five membered ones.

3. The rate of conversion of the xylenes depends on the position of the methyl groups in the nucleus and increases in the order m-xylene < p-xylene < o-xylene.

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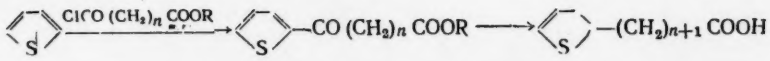
THE SYNTHESIS OF ω-THIENYLALKANE* ACIDS FROM ω-CHLOROALKANE ACIDS

L. I. Belen'kii, S. Z. Taits, and Ya. L. Gol'dfarb

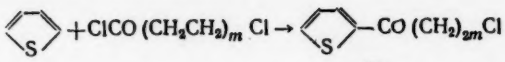
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1706-1708, September, 1961

ω-Thienylalkane acids which we used as starting compounds for the synthesis of macrocylcic compounds [1] were obtained by the scheme:



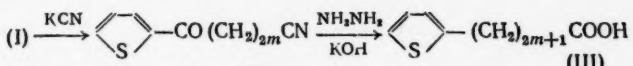
By this method we synthesized acids with n = 2,3,4,7,8, but the synthesis of other thienyalkane acids was difficult due to the slight availability of the corresponding dicarboxylic acids. In the present communication we describe a suitable process for the synthesis of ω-thienylalkane acids in which the starting substances are thiophene and ω-chloroalkane acids of the type Cl $(CH_2CH_2)_m$COOH which are obtained industrially from products of telomerization of ethylene with carbon tetrachloride [2,3].

The first step in this synthesis is the acylation of thiophene by ω-chloroalkane acid chlorides



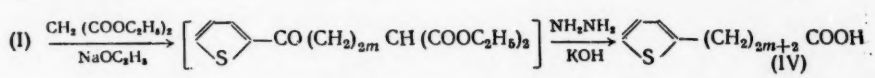
(I)

From the thus formed ω-chloroalkyl(2-thienyl)ketones we can obtain ω-thienylalkane acids with an even or odd number of carbon atoms in the aliphatic chain. In the first case the chloroketone (I) is treated with cyanide with later reduction of the cyanoketone (II) and simultaneous hydrolysis:



(II) (III)

Here there is no need to isolate the ω-cyanoalkyl(2-thienyl)ketone (II) in pure form. The corresponding acid (III) is obtained in yields of 75-85% calculated on the ω-chloroalkyl(2-thienyl)ketone (I). To obtain ω-thienylalkane acids with an odd number of carbon atoms in the aliphatic chain, the ω-chloroalkyl(2-thienyl)ketone is condensed with sodium malonic ester and the product, without isolation in pure form, is submitted to reduction with simultaneous hydrolysis and decarboxylation:



(IV)

The yield of acid (IV) is 50-75%. By this method we have synthesized from the ω-chloroalkane acids the little available ω-thienylalkane acids (III) and (IV) with m = 2,3,4,5.

EXPERIMENTAL

Obtaining ω-Chloroalkyl(2-thienyl)ketones (I). To a solution of 0.1 M ω-chloroalkane acid chloride** and

*Here and later we mean ω-(2-thienyl)alkane acids.

**The chlorides were obtained with yields of 90-95% by the action of the corresponding acid with thionyl chloride followed by distillation. We used acid chlorides of the following acids: 5-chlorovaleric, b.p. 82-85° (10 mm); 7-chloroenanthic, b.p. 87-89° (2 mm); 9-chloropelargonic, b.p. 113-115° (1.5 mm); 11-chloroundecanoic, b.p. 128-132° (0.75 mm).

TABLE 1. ω-Chloroalkyl(2-thienyl)ketones [1]* Semicarbazones

m	B. p., °C (p, mm Hg)	M.p., °C	Yield, %	Found, %				Empirical formula	Calculated, %				M. p., °C	found, % N	Empirical formula	Calcu-lated, % N
				C	H	S	Cl		C	H	S	Cl				
2	110—116(0,1)	38—39	92,5	53,27	5,39	15,67	17,43	$C_9H_{11}ClOS$	53,28	5,47	15,82	17,49	148—149	15,92	$C_{10}H_{14}ClN_3OS$	16,70
3	132—134(0,3)	28—30	89,0	57,23	6,43	13,89	15,51	$C_{11}H_{15}ClOS$	57,25	6,55	13,90	15,37	123—124	14,61	$C_{12}H_{16}ClN_3OS$	14,60
5	193—197(1,0)	39—40	78,6	63,00	8,14	10,95	11,99	$C_{15}H_{25}ClOS$	62,80	8,08	11,18	12,36	108,5—109,5	12,18	$C_{16}H_{26}ClN_3OS$	12,22

* ω-Chlorooctyl(2-thienyl)ketone (I) (m = 4) and its semicarbazone were described previously by us [7].

0.1 M of thiophene in 100 ml of dry benzene at 3-5° with stirring we added a solution of 0.1 M tin chloride in 20 ml of benzene, after which without cooling it was stirred for an hour more. The mixture was treated with 50 ml of dilute (1:10 by volume) hydrochloric acid at a temperature not above 10°; the benzene layer was washed with water, with a soda solution, and again with water; the benzene was distilled off and the residue was distilled in a vacuum. The constants and yield of reaction products are given in Table 1.

Obtaining ω-Thienylalkane Acids with Even Number of Carbon Atoms in the Aliphatic Chain (III). The action of cyanide on ω-chloroalkyl(2-thienyl) ketones was carried out under conditions analogous to those described by Nesmeyanov, Zakharkin, and Kost [4]. A mixture of 0.1 M ω-chloroalkyl(2-thienyl)ketone (I) and 0.15 M potassium cyanide was boiled for four hours in 100 ml of 80% ethyl cellosolve (or methyl cellosolve) in the presence of 1-2 g of potassium bromide, diluted with three volumes of water; the precipitate of ω-cyanoalkyl(2-thienyl)ketone (II) was filtered off* and without further purification was submitted to reduction with simultaneous hydrolysis under conditions similar to those described by Huang-Minlon [5] for the reduction of ketones. For this purpose, the unpurified cyanoketone (0.1 M) was boiled for 2-3 hours with hydrazine hydrate (0.35 M) and potassium hydroxide (0.35 M) in 200 ml of diethylene glycol, then the water and hydrazine hydrate were distilled off to a temperature in the mass of 205-215°, and it was boiled for five hours at this temperature. The mixture was diluted with water, acidified, and the acid filtered off. If the acid precipitated as an oil, it was extracted with ether or chloroform, and after removal of the solvent was distilled. The constants and yields of the ω-thienylalkane acids (III) are given in Table 3.

Obtaining ω-Thienylalkane Acids with Odd Number of Carbon Atoms in the Aliphatic Chain (IV). The malonic synthesis was carried out under the conditions described by Nesmeyanov and Zakharkin [6] for esters of chloroalkane acids. We boiled 0.1 M of ω-chloroalkyl(2-thienyl)ketone (I) for six hours in 100 ml of absolute alcohol in the presence of 2-3 g of anhydrous sodium iodide with preliminary preparation of sodium malonic ester (0.12 atoms of sodium and 0.15 M malonic ester). The alcohol was distilled off, the mixture was diluted with water and extracted with benzene. The benzene and excess malonic ester were distilled off (at the end in a vacuum of a water pump), and the residue without isolation of the product was treated with hydrazine hydrate and potassium hydroxide under the conditions described above. The constants and yields of ω-thienylalkane acids are given in Table 3.

We take this opportunity to thank R. Kh. Freidlina, A. A. Beer, and M. A. Besprozvannii for giving us enough ω-chloroalkane acids.

SUMMARY

We have worked out a preparative method for the synthesis of ω-thienylalkane acids by acylation of thiophene with ω-chloroalkane acid chlorides followed by conversion of the resulting ω-chloroalkyl(2-thienyl)ketones into the corresponding acids by reaction with sodium malonic ester or potassium cyanide, and reduction of the resulting products with their simultaneous hydrolysis.

* ω-Cyanoalkyl(2-thienyl)ketones were purified by recrystallization from alcohol and n-heptane, and their melting points and yields are given in Table 2.

TABLE 2. ω-Cyanoalkyl(2-thienyl)ketones (II)

m	M. p., °C	Yield, %	Found, %			Empirical formula	Calculated, %		
			C	H	S		C	H	S
3	50,5—52,5	79,0	65,00	6,55	14,35	$C_{12}H_{15}NOS$	65,12	6,83	14,49
4	53—54,5	98,5	67,21	7,38	12,95	$C_{14}H_{19}NOS$	67,43	7,68	12,86
5	63—64	93,5	69,36	8,28	11,48	$C_{16}H_{23}NOS$	69,27	8,35	11,56

TABLE 3. ω-Thienylalkane Acids (III) and (IV)

Acid	B. p., °C (p, mm Hg)	M. p., °C	Yield, %	M. p., °C from literature
7-Thienylenanthoic	148—152(0,2)	28—30	72,5	30[8]
8-Thienylcaprylic	147—150(0,03)	14,2—15.6	74,5	15[9]
10-Thienylcapric	170—175(1,5)	33—34	76,5	33—33,8[1]
11-Thienylundecanoic	165—170(0,05)	47—48,5	51,5	42[8]
12-Thienyllauric*	200—205(0,1)	39,5—40,5	86,6	—
13-Thienyltridecanoic**	—	57,5—59	50,0	—

* Found: C 68.00; H 9.15; S 11.40%. $C_{16}H_{26}O_2S$. Calculated: C 68.04; H 9.28; S 11.35%. The palmitic acid obtained by the action of skeletal nickel gives no melting point depression with a known sample.

** Found: C 68.79; H 9.38; S 10.82%. $C_{17}H_{28}O_2S$. Calculated: C 68.85; H 9.52; S 10.82%. Amide, m.p. 99.5-101.5°; found: N 4.82%. $C_{17}H_{23}NOS$. Calculated: N 4.74%.

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AN APPARATUS FOR MIXING HETEROGENEOUS SYSTEMS AND MEASURING THE APPARENT VOLUME OF PRECIPITATES OR LAYERS OF LIQUIDS

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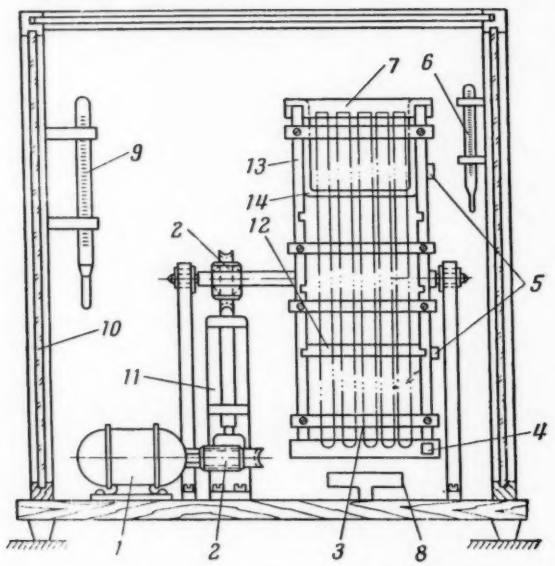
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9,
pp. 1709-1710, September, 1961
Original article submitted March 21, 1961

In 1950 Tananaev [1] suggested as a new method for study by physicochemical analysis of chemical systems the measurement of the apparent volume of a precipitate. The method which Tananaev suggested for this is not sufficiently good (absence of thermostatic control, hand stirring). In 1960 [2] we suggested studying a chemical system simultaneously by the method of solubility and apparent volume of precipitate, using the same vessel (with thermostatic control and mixing with an electric motor).



Scheme in principle of apparatus: 1) electric motor; 2) worm drive; 3) measuring cylinders (test tubes); 4) level; 5) equalizers; 6) thermometer; 7) cover; 8) heater; 9) contact thermometer; 10) glass case; 11) support for worm drive; 12) movable bottom; 13) frame; 14) U-shaped guide rack.

The apparatus which we suggest in this case (see diagram in the figure) is intended for work separately or together of the methods of solubility, apparent volume of precipitate, and other methods of physicochemical analysis. The apparatus speeds up the work, is simple to build, and is comparatively quiet. Aside from chemisty, the apparatus can be used in medicine, physics, and other cases of laboratory practice such as for uniform stirring of liquids in solid-liquid systems, for reaching equilibrium (saturation in salt and other systems, for measuring the volume of

precipitates or layers of liquids in separating liquid systems, etc. This apparatus has justified itself in the laboratory of the chemistry and analysis of rare elements of the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, USSR.

Scheme in principle of the apparatus. The apparatus is a rotating support with the amount of space needed in it for the measuring cylinders (test tubes) which are closed by stoppers. On an iron base (plate) standing on four rubber stoppers screwed to it and a felt cushion is fastened motor 1 and two supports. On the axis of the supports is fastened the rotating holder 13 in the form of a right angle rack. On the two longitudinal walls of the frame there are grooves where, depending on the height of the cylinders, there is inserted a plate, the sliding bottom 12. At the top of the frame, between the walls, there is inserted the U-shaped guide rack 14 which has openings in the bottom for cylinders of various diameters. The graduated cylinders 3 of glass (or other transparent material), filled with the substance to be mixed, are covered with a suitable stopper and put through the openings in the U-shaped rack on the nonsliding or sliding bottom of the frame. The cylinders are closed in with the cover 7 with a clamp or tightening screw. On the cover and at the bottom is placed padding of porous plastic sponge or fiber. It is also possible to fasten the cylinders in the frame without the guide rack, for example, by using grooves for the ends of the cylinders in the cover and on the bottom of the frame.

Movement from the motor to the axis of the frame is carried through two worm drives 2 fastened to the supports 11 which are screwed to the base. The rate of rotation of the frame, and hence the mixing of the contents of the cylinders, is regulated by an autotransformer (outside the case) depending on the diameter and height of the cylinders and assuring mixing the cylinder contents from one end to the other. For even mixing of the cylinder contents there are two movable load equalizers 5 fastened to the body of the frame.

Thermostatic control of the air during the mixing is assured by placing the apparatus in a case with glass walls 10, placing inside the case the heater 8 and the contact thermometer 9 which is connected with an electric relay (outside the case). For checking the thermostatic control inside the case we also placed an ordinary thermometer 6 there. The case was firmly held by grooves in the base and the top or front wall could be raised. After mixing the contents of the cylinders for a definite time interval, we measured the volume of the precipitate (layer of liquid), analyzed the liquid or solid phases, or measured other physicochemical properties of the system. For visual readings of the volume of precipitate (liquid) we set the frame in the vertical position using the level 4, raised the top or front wall of the case, removed the frame cover and took out the cylinders. For this purpose we could also lift off the case or, without removing it, use a visible tube. In the latter case, the fine cross strip which holds the frame is made of transparent material (plexiglas or other plastic material). By keeping in the limits 0-40° thermostatically we can use passage of cooled (heated) air, or, as a heater, an ordinary electric lamp or spiral. Also, in some cases for thermostatic control we can use a refrigerator, placing the apparatus in it and thus avoiding use of the case, heater and contact thermometer.

The use of the apparatus over a wider range of temperature depends on the materials used in its construction. For example, when raising the temperature, the cylinders and walls of the case can be made of heat resistant glass or quartz. The worm drives, motor, and supports in this case are outside the case and for construction of the rotating frame and its axis we use heat resistant materials. At high temperatures the thermometers are held in openings in the case, so that the mercury bulbs are inside and the measuring portion outside the case. It is also satisfactory to use calibrated thermocouples. For construction of the measuring cylinders, besides glass or quart, we can use any other transparent material suitable for use under these conditions (polyethylene, plexiglas, and other plastics). If the precipitate is labeled with radioactive indicators, its volume can be measured with a radiation counter, and the cylinder in this case can be made of nontransparent material, including metals or plastics. The stoppers may be glass or quartz instead of rubber. Stoppers do not have to be used; the ends of the cylinders may be sealed. The worm drive may be made of Teflon, textolite, capron, or viniplast instead of metal, which increases the quietness. The removable U-shaped guide rack can be made of sheet iron or aluminum. Except for the transparent parts, the apparatus can be made of iron or any suitable material, but the best is obviously plastic or aluminum.

SUMMARY

1. We have proposed an apparatus for mixing heterogeneous systems and at the same time for measuring the apparent volume of precipitates or layers of liquid.

2. The apparatus hastens the work, occupies little space, is comparatively noiseless, is simple to construct, and is convenient in use.

3. The apparatus can be used in chemistry, physics, medicine, and other cases.

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HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF XYLENES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1711-1713, September, 1961
Original article submitted March 22, 1961

In previous work [1-3] we have studied the homogeneous destructive hydrogenation of toluene, isopropylbenzene, and tetraline, and have suggested a general scheme for a radical-chain mechanism of this process. In the present work we will give some results on the homogeneous destructive hydrogenation of the xylenes.

TABLE 1. Yield of Benzene and Toluene in Homogeneous Destructive Hydrogenation of Xylenes in an Autoclave at 460°

P_{H_2} initial atm	$P_{working}$ atm	Mole ratio H_2/xylene	τ hours	Yield, mol. % on charge*		
				benzene	toluene	benzene + toluene
From o-oxylene						
100	280	1,0	3	0	24,7	24,7
300	700	2,8	3	8,6	45,5	54,1
500	1120	4,4	3	13,9	53,5	67,4
300	700	2,8	5	21,4	53,4	74,8
From m-xylene						
100	280	1,0	3	0	20,3	20,3
300	700	2,8	3	6,2	33,4	39,6
500	1120	4,4	3	11,0	40,3	51,3
300	700	2,8	5	14,5	42,5	57,0

* With account of loss of 1.5 g in loading the reactor and column.

TABLE 2. Yield of Benzene and Toulene in Homogeneous Destructive Hydrogenation of Xylenes in a Flow Apparatus at 195-200 atm and 557-560°

Hydrocarbon (mixture)	Temperature, °C	w, $hours^{-1}$	Mole ratio H_2/hydrocarbon	Yield, mol. % on charge		
				benzene	Toluene	benzene + toluene
o-Xylene	560	1,6	2,4	2,0	29,6	31,6
m-Xylene	558	1,7	2,2	1,3	19,7	21,0
m-Xylene + 5% o-xylene	557	1,7	2,2	3,2	21,7	24,9
m-Xylene, technical	560	1,5	2,5	13,0	35,6	48,6
m-Xylene, technical	557	1,9	1,9	11,0	32,8	43,8
m-Xylene + 5% ethylbenzene	558	1,7	2,3	5,9	27,8	33,7

EXPERIMENTAL

For the study we used xylenes characterized by the following constants: o-xylene, b.p. 144.2-144.4°, d_4^{20} 0.8800; n_D^{20} 1.5054; m-xylene, b.p. 138.9-139.1°, d_4^{20} 0.8640; n_D^{20} 1.4972. We also carried out experiments with technical m-xylene containing about 70% m-xylene, about 15% p-xylene, about 10% ethylbenzene, and about 5% o-xylene. The

experiments were carried out in an autoclave by the usual method [1] at 460° and in an apparatus of the flow type [4] at 557-560°. The reaction products were dried and distilled in a rectification column with an efficiency of 25 theoretical plates. We thus distilled off benzene, toluene, and starting xylene; the higher boiling residue (up to 5%) was not further studied. The results of some of the experiments are given in Tables 1 and 2.

From the data of Table 1 we can draw the following conclusions: a) the rate of homogeneous destructive hydrogenation of xylenes is markedly increased with rising pressure; b) demethylation of o-xylene occurs with greater speed than with m-xylene. This is also confirmed by the data of Table 2. The results of the experiments shown in Table 2 with technical m-xylene indicate that in this case homogeneous destructive hydrogenation occurs faster than with the pure xylenes. We can assume that this increased rate of reaction depends on the admixture of ethylbenzene. Actually, addition of 5% ethylbenzene to pure m-xylene (last line of Table 2) led to a marked increase in yield of benzene and toluene in one passage.

RESULTS

Homogeneous destructive hydrogenation of alkyl benzenes can be considered as an approximately bimolecular reaction between the hydrocarbon and hydrogen [5,4] and at a greater excess of hydrogen, as a pseudomonomolecular reaction. It is natural to assume that homogeneous destructive hydrogenation of the xylenes occurs in two stages: first formation of toluene, which is then demethylated with formation of benzene. Then we can attempt to describe approximately the kinetics of the homogeneous destructive hydrogenation of m-xylene by the equation for two successive pseudomonomolecular reactions

$$x = \frac{K_1}{K_2 - K_1}\left(e^{-K_1\tau} - e^{-K_2\tau}\right).$$

Here x is the yield of toluene (in mole portions of the starting xylene). K_1 and K_2 are the rate constants for demethylation of m-xylene and toluene respectively. The value of K_1 can be calculated by adding the yield of

TABLE 3. Results of Calculation by Equation (1) at $K_1 = 2K_2$

Expt. conditions			Yield (in moles on starting xylene)			
			toluene		benzene	
$P_{initial}$, atm	τ, hours	K_1	found	calculated	found	calculated
300	3	0.168	0.334	0.344	0.062	0.052
300	5	0.168	0.425	0.470	0.145	0.100
500	3	0.240	0.403	0.420	0.110	0.093

benzene and toluene (according to the usual equation of a monomolecular reaction). We can expect that the first stage of the reaction will occur about twice as fast as the second, since the probability of the occurrence of any reaction with the participation of a methyl group in the xylene should be about twice as great as in toluene, and the activation energy of demethylation should in both cases be similar in size. This suggestion is justified especially by the data on the pyrolysis of xylene and toluene. Thus, Szwarc [6] found that the energy of breaking the bond C–H in the methyl group was for toluene 77.3 kcal/M and for m-xylene 77.1 kcal/M*; according to the data of the same author the value of the exponent in the Arrhenius equation for the pyrolysis of xylenes is about twice as high as in the pyrolysis of toluene ($4\text{-}5 \cdot 10^{13}$ and $2 \cdot 10^{13}$ sec^{-1} respectively).

In Table 3 we give the results of the calculation by equation (1) at $K_1 = 2K_2$. Both these constants include the concentration of hydrogen which we took as constant for the given experiment.

It follows from Table 3 that these calculations lead to somewhat high values for the yield of toluene and can be considered only as approximations**.

* In o- and p-xylene the activation energy is lower, 74.8 and 76.2 kcal/M respectively.

** There is better agreement of caluclation with experiment at $K_1 = 1.5K_2$.

The greater rate of homogeneous destructive hydrogenation of o-xylene as compared to m-xylene which we found in the present work evidently depends on the lower energy of rupture of the C—H bond in the methyl group of o-xylene as compared to m-xylene, which confirms our previous idea of the scheme of mechanism of this process. [1,2]. The marked hastening of the reaction in the presence of small amounts of ethylbenzene also agrees with this scheme; as is known the less stable bond in the molecule of ethylbenzene is the bond $C_6H_5CH_2$-CH_3 (D = 63 kcal/M [7]); rupture of this bond occurs faster than rupture of the least stable bond ($CH_3C_6H_4CH_2$-H) in the m-xylene molecule (77.1 kcal/M), which also causes increase in rate of reaction of the resulting chain.

SUMMARY

1. Homogeneous destructive hydrogenation of o-xylene at 460 and 560° occurs faster than for m-xylene. Increase in partial pressure of hydrogen leads to a marked hastening of the reaction. The process is greatly speeded on addition to m-xylene of small amounts of ethylbenzene.

2. Splitting of the first methyl group from the m-xylene molecule occurs in one and a half to two times faster than splitting of the methyl group from the toluene molecule.

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CATALYTIC HYDROGENATION OF AROMATIC NITRILES AND THEIR PROPERTIES OF POLYAMIDES OBTAINED FROM p-(β,β'-DIAMINODIETHYLBENZENE)

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1713-1715, September, 1961
Original article submitted March 28, 1961

Aromatic diamines which contain the amino group in the side chain are important in the production of high molecular weight polyamides [1]. In previous work [2,3] we have studied the preparation of aromatic diamines by catalytic hydrogenation of dinitriles of o-, m-, and p-phathalic acids on skeletal nickel and cobalt catalysts. In the present work we report the hydrogenation of the dinitrile of p-phenylenediacetic acid into p-(β-β'diaminodiethylbenzene):

$$NC—CH_2—C_6H_4CH_2CN \rightarrow H_2N—C_2H_4—C_6H_4—C_2H_4—NH_2$$

and the properties of the polyamide obtained on the basis of this diamine.

TABLE 1

Expt. No.	Used in reaction: dinitrile, g	Used in reaction: catalyst, g	Used in reaction: solvent	Catalyzate composition, wt., %: diamide	Catalyzate composition, wt., %: residue	Hydrogenation conditions
1	p-NC−CH_2−C_6H_4−CH_2−CN, 10	Ni 7	ethanol	65	35	Temperature 100-105°, initial hydrogen pressure 100 atm, mole ratio dinitrile: ammonia 1:10, volume ratio dinitrile: solvent about 1:3.
2	same 8.8	Ni 6	methanol	64	36	
3	" " 9.5	Co 7	dioxane	74	26	
4	" " 9	Co* 8	methanol	94	6	
5	" " 10	Co* 8	dioxane	92	8	
6	p-NC−C_6H_4−CN 18	Co* 8	dioxane	65	35	
7	The same 6	Co* 3	methanol	89	11	

*Catalyst prepared by the method of "cold leaching".

EXPERIMENTAL

The dinitrile of p-phenylenediacetic acid with m.p. 95-97° (from methanol) was prepared from acetocyanhydrin and p-xylene dibromide [4]. According to the literature, m.p. 95.5-97°. Hydrogenation was carried out at 100-105° and initial hydrogen pressure of 100 atm in a rotating steel autoclave with a capacity of 0.175 liters in a medium of dioxane, methanol, or ethanol in the presence of ammonia. The catalysts were prepared by exhaustive leaching of a powder of 50% alloy of Ni-Al and Co-Al with 10% aqueous NaOH, followed by washing with water to a neutral

reaction to phenolphthalein. In a number of experiments we used a skeletal cobalt catalyst prepared by leaching an alloy with 25-30 water solutions of alkali at a temperature not above 15° [5].

The solvent was distilled from the reaction mixture which had been separated from the catalyst; then at reduced pressure in an atmosphere of nitrogen the diamine fraction was distilled with a b.p. 161-162° (7 mm); 143-145° (5.5 mm); m.p. about 60°. When a sample of 0.0562 g was titrated in the presence of a mixed indicator (methylene red and methylene blue [6]) 6.83 ml of 0.0996 N HCl was required which corresponded to a content of 99.8% of diamine. According to the literature the b.p. of p-(β,β'-diaminodiethylbenzene) is 130° (3 mm), m.p. about 60° [7]. The conditions and results of the experiments are given in Table 1, from which we see that in the presence of a skeletal nickel catalyst the yield of diamine was 64-65% (experiments 1 and 2). In the work of Ruggli and co-workers

TABLE 2

Starting monomers	No. of recrystallization of salt	Conditions of carrying out polycondensation		Characteristics of polymer		
		T, °C	Time, hours	Appearance of polymer at polycondensation temperature	m.p. of polymer, °C	relative viscosity of 1% solution of polymer in conc. H_2SO_4
Salt of adipic acid and diamine*	1	260	1	pale yellow, nonmelting block	314–320	1.93
The same	1	280	3	yellowish nonmelting block	314–320	2.10
" "	2	280	1	white nonmelting block	314–320	2.11
" "	2	280	3	the same	314–320	2.31
" "	2	280	4	" "	314–320	2.69
Adipic acid chloride, diamine**	–	20	–	white film	314–320	1.18
Sebacic acid chloride, diamine**	–	20	–	" "	235–240	1.35
Terephthalic acid chloride, diamine**	–	20	–	white powder	390°	Insol.

*p-(β,β'-diaminodiethylbenzene).

** Polymer obtained by method of heterophase polycondensation.

[7] at lower initial hydrogen pressure (75 atm) the yield of diamine was 57% The nature of the catalyst and the method of preparing it are of great significance for the yield of diamine. In the presence of a skeletal cobalt catalyst prepared by leaching at 90-100°, the yield of diamine was 74% (experiment 3), and on cobalt prepared by the method of "cold leaching" it reached 94% (experiment 4).

On hydrogenation of the dinitrile of terephthalic acid in the presence of skeletal cobalt a much greater yield of p-xylenediamine was also obtained on a catalyst prepared by leaching the alloy in the cold (89%).

We then studied the polycondensation of the resulting p-(β,β'-diaminodiethylbenzene) with adipic and terephthalic acids. When we mixed equimolecular water solutions of diamine and adipic acid and precipitated the salt with acetone, we obtained a white, crystalline substance with m.p. 200-202° (after two recrystallizations from water). Found: N 8.98%. $C_{16}H_{26}N_2O_4$. Calculated: N 9.02%.

By polycondensation of the salt at 260-280° we obtained the polyamide. It was first established that on heating to this temperature the salt did not sublime and did not decompose, which simplified carrying out the polycondensation. The reaction took place at atmospheric pressure in a stream of dry nitrogen, carefully freed from traces of oxygen. Polycondensation occurred in the solid phase at a temperature below the melting point of the polyamide. The polyamide based on p-(β,β'-diaminodiethylbenzene) and adipic acid was also obtained at a temperature of 20° by the method of heterophase polycondensation on reaction of a water solution of the diamine (with addition of soda)

and a solution of adipic acid chloride in benzene. In an analogous way we obtained the polyamide based on terephthalic acid chloride and sebasic acid chloride in a medium of methylene chloride and a water solution of the diamine with addition of soda to bind the hydrochloric acid formed by method [8].

Table 2 shows the effect of the reaction conditions on the properties of the resulting polyamide. These results show that under all the conditions studied polycondensation of adipic acid and the diamine under investigation forms a polyamide with m.p. 314-320°, soluble in concentrated H_2SO_4, insoluble in cresol (even at 100°), formic, and hydrochloric acids and organic solvents. Increased temperature and longer duration of the reaction lead to increase in molecular weight of the resulting polyamide: the relative viscosity of the polyamides in concentrated H_2SO_4 rises from 1.73 to 2.69.

Spinning the high molecular polyamides from the melt at temperatures of 335-340° gave fibers capable of orientation at high temperatures. The properties of the polymers also depend on the quality of the starting salt: in the case of a single recrystallization of the salt a colored polyamide with lower molecular weight is formed.

SUMMARY

1. We have studied the hydrogenation of the dinitriles of p-phenylenediacetic and terephthalic acids on skeletal catalysts. A skeletal cobalt catalyst prepared by leaching in the cold has considerably greater selective action than that obtained by leaching with heating.

2. Polycondensation of the salt of p-(β,β'-diaminodiethylbenzene) and adipic acid gives a high molecular weight fiber forming polyamide with m.p. 314-320°.

3. We have studied the properties of the polyamides based on p-(β,β'-diaminodiethylbenzene) and sebacic and terephthalic acids.

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LETTERS TO THE EDITOR

SULFONATION OF CYCLOPENTADIENYL COMPOUNDS OF ZIRCONIUM

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1716, September, 1961
Original article submitted June 22, 1961

We report that according to our results, the dichloride of dicyclopentadienyl zirconium (I) can react by electrophilic substitution. On reaction of (I) with a mixture of sulfuric acid and acetic anhydride we obtained the dibisulfate $[(C_5H_5)(C_5H_4SO_3H)Zr(OSO_3H)_2] \cdot (CH_3CO)_2O$ (II) which contained one molecule of acetic anhydride. Found: C 28.08; 28.39; H 3.29; 3.14; S 15.81; 16.25%. $C_{14}H_{18}O_{14}S_3Zr$. Calculated: C 28.12; H 3.03; S 16.07%.

Compound (II) is nonmelting, hydroscopic, and insoluble in most organic solvents; soluble in alcohols. On reprecipitation from solution in absolute ethyl alcohol by ligroin we obtained a double compound of dibisulfate with alcohol $[(C_5H_5)(C_5H_4SO_3H)Zr(OSO_3H)_2] \cdot C_2H_5OH$ (III). Found: C 27.11; 26.96; H 3.18; 3.19%. $C_{12}H_{18}O_{12}S_3Zr$. Calculated: C 26.61; H 3.32%.

In compounds (II) and (III) we showed the presence of only one unsubstituted cyclopentadienyl group which was quantitatively isolated in the form of thallium, cyclopentadienyl.

The action of acetylacetone on (II) led to a compound with the composition $[(C_5H_7O_2)(C_5H_4SO_3H)Zr(SO_4H)] \cdot C_5H_8O$ (IV). Found: C 38.13; 38.09; H 4.16; 4.34; S 10.69; 11.04%. $C_{20}H_{28}O_{12}S_2Zr$. Calculated: C 38.01; H 4.46; S 10.14%.

This reaction is analogous to those of the dichloride of dicyclopentadienyl zirconium with acetyl acetone in which there is formed a compound of the composition $(C_5H_7O_2)_2C_5H_5ZrCl$ [1].

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THE REACTION OF ATOMIC HYDROGEN WITH SOLID ACETYLENE AT A TEMPERATURE OF 77°K

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1716-1717, September, 1961
Original article submitted June 22, 1961

It is known that atomic hydrogen adds quite easily to the simplest olefins frozen at the temperature of liquid nitrogen [1-4]. We have shown that atomic hydrogen, formed in the gas phase by dissociation of a H_2 molecule on a hot tungsten wire, can react with solid acetylene, frozen on the inner walls of a reaction vessel at a temperature of 77°K. The experimental method was the same as in the above work.

Mass spectrometric analysis showed that the chief product of the reaction was ethane. Evidently the mechanism of the reaction consisted in successive addition to the acetylene molecule of four atoms of hydrogen:

$$CH{\equiv}CH \xrightarrow{+H^{\cdot}} CH_2{=}\dot{C}H \xrightarrow{+H} CH_2{=}CH_2 \xrightarrow{+H^{\cdot}} CH_3{-}\dot{C}H_2 \xrightarrow{+H} CH_3{-}CH_3.$$

The rate of absorption of atomic hydrogen by a layer of solid acetylene was about 20 times below the rate of absorption of hydrogen atoms by solid propylene under the same conditions.

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A NEW METHOD FOR PREPARING CYCLIC SILICOORGANIC COMPOUNDS

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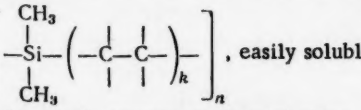
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1717, September, 1961
Original article submitted June 27, 1961

We have found that the reaction of dimethyldichlorosilane with lithium in tetrahydrofuran (THF) at 10-70° in the presence of styrene (mole ratio to $(CH_3)_2SiCl_2$ 2:1) leads to formation of diphenyldimethylsilicacyclopentane (probably a mixture of isomers); yield 30-50%; b.p. 127-129° (0.2 mm) and 136-137° (0.2 mm); n^{20}_D 1.5722-1.5759; d^{20}_4 1.0077-1.0133; found MR 86.99-87.20; calculated MR 86.69; (cryoscopic in benzene) 262, 257; calculated molec. wt. 266. Found: 81.02; 80.90; H 8.60; 8.32; Si 10.40; 10.43%. $C_{18}H_{22}Si$. Calculated: C81.15; H 8.32; Si 10.53%. Here there is also formed a considerable amount of tarry silicon-containing polymer with the probable structure

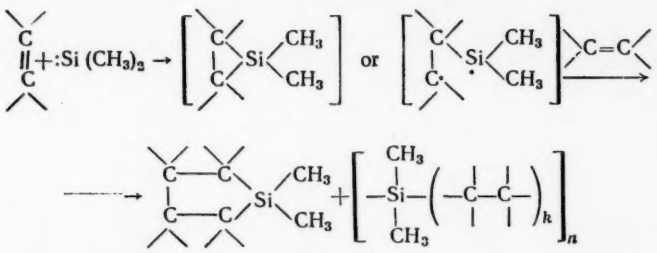


, easily soluble in acetone and other solvents. We have found a similar reaction with the substituted styrenes vinylnaphthalene, divinylbenzene, and also with methylmethacrylate. Under the same conditions, but in the absence of unsaturated compounds there is formed chiefly the high molecular weight polydimethylsilylene $\left[>Si(CH_3)_2\right]_n$; yield 65-75%; m.p. 340-345° (with decomposition). The latter differs from the similar polymer obtained earlier [1] from $(CH_3)_2SiCl_2$ and sodium in benzene (200°, 15-20 atm), being considerably more thermooxidatively stable.

We assume that the above reaction occurs through a stage of intermediate formation of dimethylsilylene, the silicon analog of the carbenes

$$(CH_3)_2SiCl_2 \xrightarrow[\text{THF}]{Li} (CH_3)_2SiLiCl \xrightarrow{-LiCl} (CH_3)_2Si:$$

The latter in the absence of an olefin polymerizes into $[>Si(CH_3)_2]_n$, but in the presence of one evidently adds first at the multiple bond with formation of an unstable silicon analog of cyclopropane or the corresponding biradicals which with excess olefin form derivatives of silicacyclopentane and polymers:



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SYNTHESIS AND PROPERTIES OF ARYLFLUOROSILICON HYDRIDES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1718, September, 1961
Original article submitted July 19, 1961

We have worked out a simple method for preparing a new type of silicon hydrides, arylfluorosilicon hydrides by reaction of the corresponding arylchlorosilicon hydrides with concentrated hydrofluoric acid at temperatures of -30-50°: $R_nCl_{3-n}SiH + 3-nHF \rightarrow R_nF_{3-n}SiH + 3-n\ HCl$.

The time of contact of the reacting substances is 20-30 minutes. With a shorter time of contact we also obtain products with substitution of only one chlorine atom by fluorine. The yields of arylfluorosilicon hydrides are 70-90%.

The reaction of arylfluorosilicon hydrides with water, alcohols, acids, without any catalyst even at room temperature leads to separation of hydrogen and formation of the corresponding silanols, alkoxy, or acyloxysilanes. Separation of hydrogen also occurs at the phase boundary when potassium fluoride, calcium chloride, metallic potassium or sodium are placed in the arylfluorosilicon hydrides. The arylfluorosilicon hydrides are initiators of polymerization in some unsaturated compounds. For example, addition of some milliliters of phenyldifluorosilane or diphenylfluorosilane at 70-80° to styrene or acrylonitrile causes their rapid polymerization. In the reaction of addition to unsaturated compounds in the presence of 1-2 weight % of 0.1 M solution of H_2PtCl_6 the arylfluorosilicon hydrides have much greater reactivity than the analogous arylchlorosilicon hydrides.

NEWS ITEMS

CONFERENCE ON THE STRUCTURE OF THE MENDELEEV PERIODIC SYSTEM

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9, pp. 1719-1720, September, 1961

March 2, 1961 in Moscow in the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR there was held a conference on the structure of the periodic system of the elements held at the initiative of the primary organization of the D. I. Mendeleev All-Union Chemical Society, the Moscow State University, and the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR. In the work of this conference 178 members of the Chemical Society took part, including instructors and scientific workers in the higher schools, institutes of the Academy of Sciences of the USSR, and various establishments of Moscow.

In his short introductory speech, Academician I. P. Chernyaev touched on the contemporary state of knowledge of the elements and their properties. He emphasized the importance of coordinating the useful problems connected with placing some elements in definite groups or subgroups.

Academician V. I. Spitsyn (Moscow State University) began with a talk on the placement of elements of the third group in the Mendeleev periodic system. He emphasized the difficulty of treating the membership of some elements in the main or subsidiary subgroup of this group. In his talk the author expressed the opinion of the need for a detailed valid assignment the analogs of boron and aluminum in the subgroup of gallium or scandium. The main guiding idea in the placement of elements in subgroups, in the opinion of the speaker, should be the idea of Mendeleev that "in groups of analogous elements the elements with the greatest atomic weight have the most sharply shown basic character or form weaker acids". Starting from this position, V. I. Spitsyn discussed analogies in the third group. Comparing gallium with boron and aluminum, he showed that on comparison of the dissociation constants of aluminum and gallium hydroxides there was a decrease in basic properties of the latter and so taking gallium as the closest analog of aluminum contradicts the Mendeleev rule. A different picture is found by comparing the properties of aluminum hydroxide with scandium and yttrium hydroxides. Here there is full agreement with the Mendeleev rule. This, gallium, indium, and thallium should be assigned to the subsidiary subgroup.

The author showed further that the formal sign, the beginning of filling up the electrons of the d-sublevel of the atom, is not a sufficient argument for assigning an element of the scandium subgroup to the subsidiary subgroup of the third group, since in the ionic state the higher valences resemble each other more in the structure of the atom for elements of the short periods and the first half of the long periods. Thus, ions of the elements of the scandium subgroup, characterized by electron shells of the type of the inert gases, are more like the ions of aluminum and boron than the ions of the subgroup of gallium, which have an eighteen electron shell. The chief guiding principle in arranging the elements of all groups of the periodic table into main and subsidiary subgroups, as the speaker emphasized, should be the relation of the chemical properties of the elements. On the basis of this criterion we should assign to the chief subgroup of the third group, along with boron and aluminum, the elements of the scandium subgroup.

In the second address, given by Prof. A. V. Lapitskii (Moscow State University), he touched on the problem of the arrangement of the cis- and transuranium elements in the periodic system of the elements. He considered in detail the current conception of the actinides and showed the contradictions in the arguments of the supporter of this view, Seaborg. Concerning the views of Gaisinskii on the nature of the cis- and transuranium elements, the speaker showed the lack of strictness in the ideas of the author on the classification of the heavy elements which assigned uranium, neptunium, plutonium, and americium to the "uranides" and curium and the following elements to the "curides". Lapinskii showed that such a division is not firmly based and to a considerable extent has a formal character.

Starting from the basis of the position of Mendeleev, the speaker suggested in considering the assignment of the transuranium elements to definite groups that we be guided by the chemical properties. Emphasizing the many valence state of the transuranium elements, Lapitskii stated that by starting only from the chemical properties of the

transuranium elements we could classify them as uranides, protoactinides, thorides, and actinides. However, based on the most typical valence state of thorium, protoactinium, and uranium, the speaker showed that these elements were not placed by chance in the fourth, fifth, and sixth groups by Mendeleev. This was in strict agreement with the geochemical characteristics of these elements. Considering the characteristics of the electron configuration of the atoms of the last series in the periodic system, in the opinion of the speaker, these elements must be assigned to the actinides. In the table of the elements this should be reflected in the following amendments: thorium, protoactinium, and uranium should remain in the places assigned to them by Mendeleev, but these elements should be put among the actinides which would emphasize their membership in the 5-f family.

In a paper on "The Periodic Law of Mendeleev and the Form of Its Expression", Corresponding Member, Academy of Sciences, USSR, G. B. Bokii (Moscow State University) stated that the main consideration for the periodic law should be: a) the content of groups and subgroups in the periodic system; b) the naming and arranging of the groups and subgroups relative to each other. By the content of subgroups (groups) is meant the enumeration of all the elements which compose a given subgroup or group. Consideration of the question led basically to establishing the position in the table of hydrogen, beryllium and magnesium, boron and aluminum, carbon and silicon, and also the actinides. In discussing the methods which could solve these questions, in the opinion of Bokii, the crystallochemical method has an advantage over the chemical and physicochemical. The deficiency of the physical method is that it cannot assure a single arrangement of the elements in the periodic table.

Chemical methods have an analogous deficiency, since the properties of the elements are determined in the process of a chemical reaction, that is, certainly with the participation of other chemical elements, and these affect the properties of the ones being studied. The crystallochemical method does not have these deficiencies, since in the structure of a simple substance it is concerned only with the reaction of a given chemical element with atoms of the same element. The results obtained by this method, therefore, are well defined. On the basis of crystallochemical data the speaker suggested assigning hydrogen to the seventh subgroup, and boron and aluminum to the third subgroup. Discussing the argument of Spitsyn on assigning the scandium subgroup to the analogous elements boron and aluminum, the speaker did not agree with such treatment, and on the basis of crystallochemical data suggested assigning scandium, yttrium, lanthanum, and actinium to the subsidiary subgroup. In conclusion, Bokii discussed the relation between the groups eight and zero and suggested including the elements of group zero in group eight, thus creating two subgroups.

The paper of V. I. Semishin (Moscow Institute of Chemical Machine Construction), "The Argon Elements and the Periodic Law of D. I. Mendeleev" was devoted to the question of the history of the discovery of the inert gases and their placement in the periodic system of the elements. The speaker discussed in detail the work of N. Morozov, who predicted the existence of the inert gases. He also described the views of Mendeleev, Brauner and others on the nature of argon. The accumulation of information on the new inert gases, the discovery of helium and the other inert gases, and the study of their physicochemical properties led to the recognition of the reality of existence of these elements. Semishin also described the ideas of Crookes, Ramsay, and Beketov on the placement of the inert gases in the eighth group; at last Mendeleev placed the argon elements in the zero group. The speaker explained the chemical nature of the different compounds of elements of group zero. He gave a critical discussion of the ideas of N. A. Figurovskii and B. M. Kedrov on the possibility of a prediction by Mendeleev of the existence of a zero group of elements and demonstrated the error of their conclusions. Finally, disagreeing with Bokii, Semishin favored keeping the zero group in the periodic system of the elements.

These summarized papers evoked great interest among the participants in the conference and produced lively discussions. A. V.Solov'ev (Moscow Steel Institute), A. A. Taperova (Moscow Steel Institute), Academician I. I. Chernyaev and A. A. Makarenya (Leningrad State University, D. I. Mendeleev Archives) emphasized the importance and timeliness of holding this conference. V. I. Spitsyn, N. I. Moskvitin (Moscow Wood Institute) and G. B. Bokii favored keeping thorium and uranium in the fourth and sixth groups. In the opinion of A. V. Novoselova the transuranium elements should be assigned to the actinides in recognition in them of the presence of their 5-f electrons. V. I. Spitsyn and G. P. Luchinskii (Moscow Machine Tool-Instrument Institute) favored retaining the zero group. In the opinion of the latter, hydrogen should be placed in the first group. Most of the participants spoke of the need for constructing in addition to the usual short form of the Mendeleev table of the elements, a variant with development of the long periods.

On the basis of the discussions, the conference passed the following resolutions.

1. In addition to the short table it is desirable to construct a system of the elements of Mendeleev with development of the long periods. The directors of the Mendeleev All-Union Chemical Society are asked to appeal to the Goskhimizdat to publish a widely circulated developed form of the table.

2. It is considered desirable to call a wider conference on the structure of the periodic system with attendance of chemists from othr branches of the All-Union Chemical Society to consider solution of the problems discussed by the present conference: 1) on the position of hydrogen; 2) on the position of the zero group; 3) on the structure of group IV; 4) on the arrangement of the actinide elements.

A. V. Lapitskii

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
	Life Sciences	Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
	Life Sciences	Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
	Life Sciences	Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
	Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
	Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
	Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
	Earth Sciences	Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
	Earth Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
	Earth Sciences	Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
	Mathematics	Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
	Physics	Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
	Physics	Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1 1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1 1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1 1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (In English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48 1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4 1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1 1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1 1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1 1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimli	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. –Publisher.